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# PROCEEDINGS OF THE ROYAL SOCIETY.

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## SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCE

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### *On the Velocity of Sound in Gases at High Temperatures, and the Ratio of the Specific Heats.*

By HAROLD B. DIXON, C.B.E., F.R.S., COLIN CAMPBELL, D.Sc., and  
A. PARKER, D.Sc.

(Received May 20, 1921.)

The experiments described in this memoir on the velocity of sound in gases, at temperatures varying from atmospheric to that of a bright red heat, were made with the object of tracing the change in the specific heat of gases with rising temperature, and, if possible, of arriving at formulæ which might be applicable to the extremely high temperatures reached in explosions. The sound method was decided on chiefly for the reasons (1) that the velocity of sound in a heated gas gives a value for the ratio of the two specific heats at the temperature of the experiment, and not as in the method of mixtures at a mean temperature between the highest and lowest point of the heated and cooled gas; and (2) because we had had considerable experience in the use of a chronograph for measuring the rapid movements of flame through gases in long tubes.

It is necessary to make it clear at starting that no claim is made that these experiments give more exact determinations of the specific heat of gases than those given previously by experiments over low ranges of temperature; the object has been to obtain by comparative measurements the general gradients of the curves rather than to find the exact value at any definite point.

The method of mixtures, in which a known volume of the heated gas is passed into a calorimeter (originally used by Delaroche\* and Bérard, and improved by Regnault† and Wiedemann‡), has been employed by Holborn§

\* 'Annales de Chimie,' vol. 85, p. 721 (1813).

† 'Mem. de l'Acad. Paris,' vol. 26, p. 1 (1862).

‡ 'Pogg. Ann.,' vol. 157 (1876).

§ 'Sitzber. Preuss. Akad. Berlin,' 1905, p. 175.



and Austin for high temperatures. Swann\* determined the specific heats of air and of carbon dioxide at 20° and 100° C. at constant pressure by measuring the rise of temperature of the gas after passing over a coil of platinum wire, heated electrically by a current of known constant value.

The most successful direct determinations of the specific heats of gases at constant volume were made by Joly.† A metal vessel, which was allowed to swing freely in an outer jacket, was carefully weighed by suspension from the pan of a delicate balance. A current of dry steam was then passed through the outer jacket, until the weight of the metal vessel had increased to a constant maximum by the condensation of steam on its surface. The difference between the values obtained when the vessel was evacuated and when full of gas gave a measure of the heat capacity of the gas itself. The method is not suitable for determinations at temperatures much higher than the boiling point of water.

With the object of determining the specific heats of gases at constant volume at very high temperatures, Berthelot‡ and Vieille and Mallard§ and Le Chatelier made use of an explosion method. They fired gaseous mixtures of known composition in metal bombs, and from the pressures registered, combined with the known heats of reaction, calculated the heat capacities of the gaseous products.

The methods of pressure-measurement have since been improved by Langen|| and by Hopkinson¶; and further improvements have been made in the explosion-method by M. Pier\*\* and by Bjerrum,†† who has calculated the specific heats of nitrogen, carbon dioxide, and steam up to 3000° from his own experiments and from those of Holborn and of Pier.

The method of adiabatic expansion originally devised by Clément‡‡ and Désormes has been improved by Röntgen§§ and modified by Lummer||| and Pringsheim. It has given good results for steam and carbon dioxide in the

\* 'Phil. Trans.,' A, vol. 210, p. 199 (1910).

† 'Phil. Trans.,' A, vol. 182, p. 73 (1892).

‡ 'Compt. Rend.,' vol. 95, p. 1280 (1882); vol. 96, pp. 116, 1218, 1358 (1883); 'Ann. Chim. Phys.,' vol. 4, p. 1379 (1885).

§ 'Ann. des Mines,' vol. 4, p. 379 (1884).

|| 'Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens, Berlin,' vol. 8 (1903).

¶ 'Proc. Inst. Mech. Eng.,' 1908.

\*\* 'Zeitsch. Phys. Chem.,' vol. 62, p. 385 (1908); 'Zeitsch. f. Electrochem.,' vol. 15 (1909); vol. 16 (1910).

†† 'Zeitsch. Phys. Chem.,' vol. 79 (1912); 'Zeitsch. f. Electrochem.,' vol. 17 (1911); vol. 18 (1912).

‡‡ 'Journ. de Phys.,' vol. 89 (1819).

§§ 'Pogg. Ann.,' vol. 148, p. 580 (1873).

||| 'Wied. Ann.,' vol. 64, p. 553 (1898).

hands of Makower\* and of Partington,† but it has not been used for determinations at high temperature.

Maneuvrier,‡ on the other hand, has used this method of adiabatic compression, measuring the volume and pressure produced by the rapid descent of a piston in a cylinder full of gas, while Clerk§ has measured the rise of temperature when a known amount of work was done on the gas in a gas engine. More recently, Crofts|| has attempted to determine the ratio of the specific heats of hydrogen, nitrogen, and carbon dioxide by measuring the minimum adiabatic compression necessary to fire electrolytic gas diluted with equal volumes of these gases, and of argon, on the assumption that the ignition temperatures of such mixtures were identical.

The first determinations of the velocity of sound in a gas were made in free air, in 1738, by Cassini, Maraldi, and La Caille, of the Paris Academy, by direct measurement. In 1829 Dulong¶ determined the velocity of sound in different gases by measuring the pitch produced by blowing an organ-pipe in the several gases—a method first suggested by Bernoulli in 1762.

Kundt's\*\* method, in which stationary waves are produced in a tube containing fine dust, has been used by Wüllner,†† Strecker,‡‡ Capstick,§§ and others. Stevens||| and Kalähne¶¶ used a resonance method suggested by Quincke. Similar methods were afterwards developed by Seebeck,\*\*\* Low,††† and by Thiesen††† and Steinwehr.

### *Experimental.*

In the experiments described in this paper, direct measurements of the time taken by a sound wave to travel through the gas, contained in a tube of known length, were made by means of a pendulum chronograph. The sound was propagated through pipes of three different materials—lead, mild steel, and silica.

\* 'Phil. Mag.' [6], vol. 5, p. 226 (1903).

† 'Physik. Zeit.', vol. 14, p. 969 (1913).

‡ 'Ann. Chim. Phys.' [7], vol. 6, pp. 321, 377 (1895).

§ 'Roy. Soc. Proc.', A, vol. 82 (1909).

|| 'Trans. Chem. Soc.', vol. 107, pp. 290, 306 (1915).

¶ 'Pogg. Ann.', vol. 16, p. 438 (1829).

\*\* 'Pogg. Ann.', vol. 135, pp. 337, 527 (1868).

†† 'Wied. Ann.', vol. 4, p. 321 (1878).

‡‡ 'Wied. Ann.', vol. 13, p. 20 (1881); vol. 17, p. 85 (1882).

§§ 'Roy. Soc. Proc.', vol. 34, p. 101 (1893).

||| 'Ann. d. Physik.', [4], 7, 285 (1902).

¶¶ 'Ann. d. Physik.', vol. 11, p. 225 (1903).

\*\*\* 'Pogg. Ann.', vol. 139, p. 104 (1870).

††† 'Wied. Ann.', vol. 52, p. 641 (1894).

††† 'Ann. d. Physik.', vol. 25, p. 506 (1908).

Preliminary experiments made in tubes up to 25 mm. in diameter showed that a sound wave traversed the length of a coiled tube—as measured along the axis—in the same time as it travelled through the tube when straight. It was not found possible to coil a lead pipe round a drum without appreciably increasing its length; so that, when a long coiled tube was employed, it was measured as it was wound on the drum layer by layer. In all cases the lengths of the tubes were measured along their axes.

In each case the tube was fitted at its two ends with exactly similar aluminium end-pieces, each of which acted as transmitter and receiver in turn. By this means the sound wave could be sent first in one direction and immediately afterwards in the other direction through the tube. By a simple switch arrangement each end-piece could be connected with either of the two magnetic styles of the chronograph, so that each style could be used alternately to mark the start and the finish of the sound wave's course. The end-pieces were closed at one end with a thin steel plate, and were fitted with a small disc of platinum, which broke an electric circuit when bent by the passing sound wave. The construction of this apparatus is shown in section in fig. 1.

The sound wave was produced by the steel tympanum (T) when struck by the hammer of the electromagnet (M). As the wave travelled along the tube

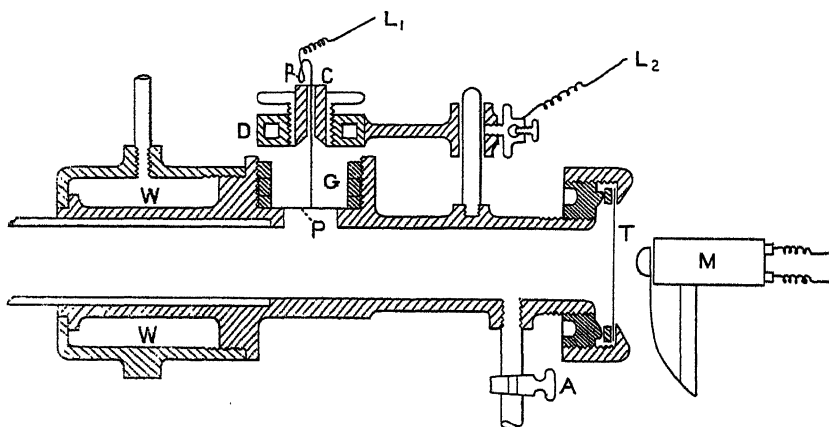


FIG. 1.

it raised the disc of platinum (P) which covered a circular opening in the aluminium; this platinum disc was kept in position by three aluminium washers, the top one of which was screwed down. A platinum upright (G), 1 cm. long, welded into the centre of the disc, carried a capillary tube of glass which passed up through the centre of a cylinder of graphite (C). The upper end of this glass tube was bent over through 180° and carried a fine

platinum wire made into the form of a loop ( $p$ ). The height of the graphite could be adjusted by means of the brass sleeve in which it was held, so as to bring it into light contact with the platinum loop, thus making connection between the two copper leads ( $L_1$ ) and ( $L_2$ ) which were in circuit with one of the chronograph styles. The whole end-piece was kept cool by a stream of cold water passed through ( $W$ ) and ( $D$ ). This cooling was necessary, since if the graphite became heated, sparking from the platinum point made indentations on its surface causing the contact to work irregularly. It was found that the efficiency of the contact was greatly increased by electroplating the graphite surface with a thin layer of copper. The gases were admitted rapidly to the tube through the tap  $A$ , until the previous contents had been completely swept out through the corresponding tap at the other end; a slow stream was then maintained under a pressure slightly above that of the atmosphere. Immediately before the experiment the taps were turned off and the platinum graphite contacts were adjusted.

The chronograph and electromagnetic styles were the same as those used by Dixon\* in his determination of the velocities of detonation waves. The chronograph consisted of a heavy pendulum which carried a smoked glass plate. The pendulum was released by a spring catch and as it passed through the lowest point of its path it caught a "break" which was in circuit with one of the hammers. The chronograph was calibrated by recording on the smoked plate the movements of a standardized tuning fork vibrating 100 times per second. By drawing an arc cutting the tuning fork marks and measuring the lengths of the chords for 1, 2, 3 or more complete vibrations, the distances corresponding with 0.01, 0.02, 0.03, etc., second, for every position on the plate, were determined and mapped out. From this "map" the value in time of any measured chord could be found by inspection. The chronograph was recalibrated from time to time with the tuning fork.

Before a sound wave was passed through the tube, a "preliminary experiment" was always performed. For this purpose, a current from two storage cells was made to pass in series through the two style magnets, the "break" on the chronograph table, and through a resistance which was so adjusted that the current passing through each magnet was of the same value in this "preliminary experiment" as in the experiments which were to follow. The pendulum was released and the consequent breaking of the circuit caused each style to rise and record its mark on the moving plate. Each mark was affected by the retardation of the corresponding electromagnet and the velocity with which the style was lifted by the spring operating it.

The first style was then connected in series with one storage cell and the

\* 'Phil. Trans.,' A, vol. 184, p. 97 (1893).

first platinum graphite contact; and the second style was similarly connected with the second contact at the opposite end of the tube. At the same time a current was made to pass in series through the electromagnet holding the first hammer and through the contact "break" of the chronograph. The pendulum was then allowed to fall, and during its path broke the circuit operating the hammer, which accordingly produced the sound wave. This wave bent the first platinum disc thereby breaking the circuit and releasing the first style. The wave then passed through the tube, bent the second platinum disc and so released the second style. The two marks recorded were affected by the same retardations as in the preliminary experiment. The distance between the two marks made by the first style represented the interval of time between the releasing of the hammer and the raising of the first disc; and the distance between the marks of the second style represented the time interval between the release of the hammer and the raising of the second disc. The difference between these time-intervals was, therefore, the time taken by the sound wave to travel from the first disc to the second. The experiment was repeated by sending the sound wave from the other end of the tube. The connections were then rearranged so that the first style was in series with the second contact and the second style in series with the first contact, and the sound wave was again measured in both directions.

The mean of the four experiments gave one determination in which all errors due to magnet and spring retardations were eliminated. Several determinations in close agreement were required before any series of experiments was considered satisfactory.

#### *Preparation of the Gases.*

*Nitrogen* was prepared by slowly dropping a concentrated solution of sodium nitrite into a hot concentrated solution of ammonium sulphate containing potassium dichromate. The gas was purified by passing through dilute sulphuric acid to remove ammonia and through ferrous sulphate to remove oxides of nitrogen, and was dried by calcium chloride and concentrated sulphuric acid.

*Carbon dioxide* was obtained from dilute hydrochloric acid and marble chippings; it was washed free from acid by sodium carbonate solution and was dried by calcium chloride and concentrated sulphuric acid.

*Nitrous oxide* was prepared by carefully heating pure ammonium nitrate, and was purified by washing with ferrous sulphate solution and drying with calcium chloride.

*Methane* was prepared by the decomposition of comparatively pure

aluminium carbide with hot water, and was purified according to the method described by Campbell\* and Parker.

*Ethane* was prepared by the action of water on magnesium ethyl iodide, and also by the action of ice-water on zinc ethide.

*Argon* was obtained from the atmosphere by first passing air freed from moisture and carbon dioxide over heated copper turnings; the remaining gas was then passed into a previously evacuated cylindrical iron vessel containing a finely powdered mixture of nine parts by weight of calcium carbide and one part of calcium chloride. The iron vessel was heated to about 800° C. in an electric furnace. The unabsorbed gas was pumped off and passed over heated calcium, to remove the last traces of oxygen and nitrogen. The resulting gas (which was practically pure argon) was stored over mercury and no attempt was made to remove the small quantities of other inert gases present. Density determinations of the product confirmed the absence of any appreciable quantity of light gases.

#### *Experiments in Lead Tubes.*

For experiments up to 100° C. it was most convenient to use a coil of lead pipe immersed in a large iron water-bath, which could be heated to the boiling point by a ring of gas-burners. The two ends of the pipe emerged through slots in the lid just far enough to make junction with the cooled end-pieces, the exposed portions of the lead (only a few centimetres) being wrapped in asbestos. In experiments made above the room temperature the mean time-intervals recorded on the chronograph were corrected for the distance travelled by the sound in the two cooled end-pieces.

As an illustration of the readings obtained, we may instance the determination of the velocity of sound in carbon dioxide at 100° C., measured in a lead pipe 25 mm. in diameter. In the readings under A and A<sub>1</sub> the sound was sent in one direction through the tube, in those under B and B<sub>1</sub> the sound was sent in the other direction; between A and A<sub>1</sub> and between B and B<sub>1</sub> the chronograph connections were reversed. After each group of four readings had been taken, a fresh smoked plate was inserted in the pendulum and the process repeated—care being taken that the tracings were, as nearly as possible, in the same positions on the plate:—

\* 'Trans. Chem. Soc.,' vol. 103, p. 1292 (1913).

June 16, 1914.	A.	B.	B <sub>1</sub> .	A <sub>1</sub> .	Mean.
					mm.
Time—4 h. 10 m. ....	190·0 29·9	192·1 30·1	190·9 28·6	189·1 29·9	
	160·1	162·0	162·3	159·2	= 160·90
Time—4 h. 15 m. ....	189·5 30·0	190·6 29·4	190·6 29·4	188·5 28·4	
	159·5	161·2	161·2	160·1	= 160·50
Time—4 h. 21 m. ....	190·6 30·5	191·6 30·0	190·6 29·1	189·9 29·9	
	160·1	161·6	161·5	160·0	= 160·80
Time—4 h. 31 m. ....	190·0 30·0	192·1 30·0	190·0 29·0	188·0 28·5	
	160·0	162·1	161·0	159·5	= 160·65
Time—4 h. 36 m. ....	188·0 28·5	191·4 30·0	191·5 29·3	189·2 29·3	
	159·5	161·4	162·2	159·9	= 160·75
Average .....					160·72

It was not found necessary to calculate the rate from each of the five sets of markings, as their respective positions on the several plates were practically the same; it was sufficient to take the *mean* distance traversed by the pendulum per 0·01 second (while the styles were tracing these marks) in order to calculate the velocity of the sound wave from the average of the group-readings. Thus the length of the tube being 18·91 metres, and the mean distance traversed by the pendulum per 0·01 second being 25·30 mm., the average velocity of sound in the gas per second is

$$\frac{18\cdot91 \times 0\cdot0253 \times 100}{0\cdot16072} = 297\cdot7 \text{ m.}$$

But a small correction is necessary for the two cooled ends of the pipe, of which 15 cm., or 0·8 per cent., were kept at 20° C. At this temperature the velocity of sound in carbon dioxide is 266 m.p.s., and therefore the velocity at 100° C. is:—

$$V = \frac{297\cdot7 \times 99\cdot2 \times 266}{26600 - (0\cdot8 \times 297\cdot7)} = 298\cdot0.$$

In a similar experiment, made with a slightly shorter tube and with longer cooled ends, the following readings were obtained:—

February 10, 1915.	A.	B.	B <sub>1</sub> .	A <sub>1</sub> .	Mean.
					mm.
Time—5 h. 10 m. ....	184·5 25·3	183·6 26·1	183·6 25·8	184·0 25·3	
	159·2	157·5	157·8	158·7	= 158·3
Time—5 h. 15 m. ....	183·8 25·5	182·6 25·8	182·6 25·8	183·0 24·9	
	158·3	156·8	156·8	158·1	= 157·5
Time—5 h. 18 m. ....	183·6 24·9	183·6 25·9	182·1 25·0	183·6 25·3	
	158·7	157·7	157·1	158·3	= 157·95
Time—5 h. 22 m. ....	184·0 25·1	182·7 25·6	182·7 25·5	183·0 24·2	
	158·9	157·1	157·2	158·8	= 158·0
Time—5 h. 26 m. ....	183·5 25·5	183·1 25·4	181·2 24·4	182·4 25·0	
	158·0	157·7	156·8	157·4	= 157·5
Average .....					157·85

The length of the tube being 18·58 metres, and the mean distance traversed by the pendulum per 0·01 second being 25·30 mm., the average velocity of sound per second is

$$\frac{18\cdot58 \times 0\cdot0253 \times 100}{0\cdot15785} = 297\cdot6 \text{ m.}$$

The portion of the tube outside the bath and cooled to 10° C. was 1·6 per cent. of the total length, the corrected velocity is therefore:—

$$V = \frac{297\cdot6 \times 98\cdot4 \times 262}{26200 - (1\cdot6 \times 297\cdot6)} = 298\cdot3.$$

A similar set of readings give, when corrected, a velocity of 298·7 m.p.s. So we have taken the mean of the three sets, viz., 298·3 m.p.s., as the velocity of sound in the lead tube at 100° C. In Table I are given the

Table I.—Velocity of Sound in Gases in Lead Tube.

Temperature (by mercury thermometer).	Velocity in metres per second in			
	Air.	Carbon dioxide.	Methane.	Ethane.
° C.				
10	334·4	262·2	431·8	305·8
50	355·5	279·3	454·0	325·1
100	385·1	298·3	481·7	346·5



mean velocities obtained in the lead tubes at room temperature,  $50^{\circ}\text{C}$ ., and  $100^{\circ}\text{C}$ . in air, carbon dioxide, methane, and ethane.

*Experiments in a Steel Tube.*

For higher temperatures a coiled tube of mild steel, 14.70 metres in length and 28 mm. in diameter, was used.

The steel pipe (fig. 2) was packed in fine sand and in an annular iron vessel, D, which was let down into a furnace between the central cylindrical block of fire-clay, A (12 inches in diameter), and the circular fire-clay wall, B (3 inches in thickness), attached to a sheet-iron cylinder, 2 feet 6 inches in

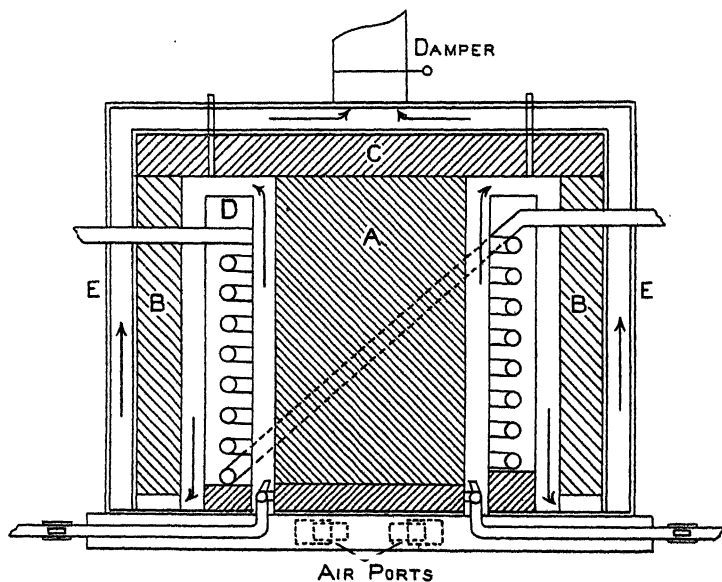


FIG. 2.

diameter. A lid of fire-clay, C, attached to an iron case rested on the top of the fire-clay centre-piece and walls. The flames from a ring of eighteen Bunsen burners passed upwards between the central fire-clay block and the tube-case, the products of combustion passing downwards between the outer side of the tube-case and the fire-clay walls. On reaching the bottom of the furnace the hot gases passed through a series of openings into an outer passage between the furnace and an asbestos-lined iron sheath, E, and so to the chimney in the middle. Through the top of the furnace iron tubes were inserted, so that the platinum resistance-thermometers might be pushed down through the sand in the tube-cases to different depths on either side.

The two ends of the steel tube were brought out of the furnace through slots in the fire-clay walls which were then made practically gas-tight by a packing of asbestos, that allowed sufficient "play" for the expansion of the tube.

The gas supply to the burners was carefully governed, and the air mixing with the gas could be regulated. The whole air supply to the furnace could be cut off by closing the air ports in the iron stand, in which a movable sector allowed access to the ring of burners. The chimney draught could be regulated or entirely stopped by a diaphragm.

The furnace, constructed by Messrs. Fletcher, Russell, and Co., was designed to maintain a temperature of  $1100^{\circ}\text{C}$ ., and this temperature could be reached with a good gas supply and the burners full on. In practice it was not found possible to keep the upper part of the tube at the same high temperature as the lower portion when the flames were burning, a difference of  $10^{\circ}$  to  $15^{\circ}\text{C}$ . being registered between the upper and lower coils. On turning off the gas the lower portion cooled more quickly than the upper, owing to the draught of cold air from below. When, however, the air supply was completely cut off by closing the air ports, the cooling was much slower, the upper portion of the coil remaining nearly constant until the lower portion had fallen to the same temperature. By raising the temperature of the lower portion some  $25^{\circ}$  above the point desired, and then turning off the gas and closing all ports, the upper and lower coils reached a common temperature some  $10^{\circ}$  above the desired point, and then cooled very nearly at the same rate.

The velocities of sound were therefore measured—during this constant cooling period—from a few degrees above to a few degrees below the standard temperature aimed at, and the mean result was taken as the velocity at that temperature.

In making the determinations one observer worked the chronograph while the second attended to the contacts and the third noted the temperature-readings, as nearly as possible at intervals of two minutes. This allowed time to make measurements of the sound in both directions at, or very close to, each recorded temperature.

The following readings were obtained with nitrogen at  $800^{\circ}\text{C}$ .,  $900^{\circ}\text{C}$ ., and  $1000^{\circ}\text{C}$ .:—

Temperature.		Mean chronograph reading.	Temperature.		Mean chronograph reading.	Temperature.		Mean chronograph reading.
$^{\circ}\text{C}$ .	mm.		$^{\circ}\text{C}$ .	mm.		$^{\circ}\text{C}$ .	mm.	
808	58.8		906	56.9		1008	54.8	
804	59.2		901	57.1		1002	55.0	
800	59.2		898	57.2		997	55.4	
790	59.4		896	57.4		992	55.1	
800		59.15	900		57.15	1000		55.08

When allowance is made for the expansion of the steel coil at  $1000^{\circ}$  and for the distance traversed by the pendulum in  $1/100$  second, the average velocity of sound in the tube is found to be

$$\frac{14.70 \times 1.012 \times 0.0256 \times 100}{0.05508} = 691.4 \text{ m.p.s.}$$

If this velocity is corrected for the cooled ends of the tube, of which it was estimated that 1.08 per cent. was at the mean temperature of  $100^{\circ}$ , then

$$V = \frac{691.4 \times 98.92 \times 390}{39000 - (1.08 \times 691.4)} = 697.3 \text{ m.p.s.}$$

The average velocity at  $900^{\circ}$  C. is given by

$$\frac{14.70 \times 1.0108 \times 0.0256 \times 100}{0.05715} = 665.3 \text{ m.p.s.}$$

and correcting for the cooled ends of the tube assumed to have a mean temperature of  $90^{\circ}$ ,

$$V = \frac{665.3 \times 98.92 \times 385}{38500 - (1.08 \times 665.3)} = 670.7 \text{ m.p.s.}$$

The average velocity at  $800^{\circ}$  C. is given by

$$\frac{14.70 \times 1.0096 \times 0.02558 \times 100}{0.05915} = 641.8 \text{ m.p.s.}$$

and correcting in a similar manner

$$V = \frac{641.8 \times 98.92 \times 382}{38200 - (1.08 \times 641.8)} = 646.6 \text{ m.p.s.}$$

Of these three determinations we felt most confidence in the value obtained at  $900^{\circ}$ ; this value was afterwards found to agree very closely with the value determined in the silica tube at  $905^{\circ}$ .

Measurements made up to  $300^{\circ}$  with other gases were corrected in a similar manner. In this way the velocity of sound in argon and nitrous oxide as well as in nitrogen were measured.

Table II contains the mean results of the experiments with nitrogen and argon.

Table II.—Steel Tube. Velocity of Sound in Nitrogen and in Argon.

Temperature (Pt. resistance thermometer).	Velocity in metres per second.	
	In nitrogen.	In argon.
$^{\circ}$ C.		
18	345.1	311.4
300	479.0	437.0
800	646.6	
900	670.7	
1000	697.3	

In Table III are given the velocities of sound in nitrous oxide as compared with the mean velocities in carbon dioxide as measured in this and in other tubes :—

Table III.—Velocity of Sound in Carbon Dioxide and in Nitrous Oxide.

Temperature.	Velocity in metres per second.	
	In carbon dioxide.	In nitrous oxide.
° C.		
20	265·0	266·0
100	297·8	299·8
200	333·4	335·6
300	364·7	369·2

*Experiments in a Silica Tube.*

Measurements at high temperatures could not be made for air and carbon dioxide owing to the action of these gases on the metal.

It was, therefore, decided to replace the iron tube by one of silica which could be heated electrically. The difficulties of making a coiled tube of silica 14 to 15 metres long, free from constrictions and strong enough to stand the necessary strains were great; but the Thermal Syndicate of Newcastle-on-Tyne decided to attempt the task. The first two tubes were broken in transit. The third arrived in good condition, was wound with platinum wire and suspended in an iron case, but broke in several places on heating.

The fourth and final tube proved more satisfactory. It was 14·5 metres long, 25 mm. internal diameter, and made into a spiral of seven complete turns, the end sections being curved outwards in opposite directions. This coil was measured into sixteen equal sections and each section was wound with the same length of platinum wire, the turns of wire being 6 mm. apart. It was then supported on four short lengths of stout silica tube, which were suspended freely inside a rectangular iron box (1·8 m. × 1·4 m. × 1·36 m.) from a horizontal cross-bar of iron (fig. A). The ends of the platinum wire were connected by leads of nichrome to two switchboards, one at the front and the other at the back of the furnace. The iron box was then filled with kieselguhr.

One end of the silica coil projected a short distance through a hole in the front of the iron case, while the other end came through the back. To each end the aluminium end-piece (already described) was attached, the joint between silica and aluminium being made with cement.

The current used for heating the coil was obtained from a 200 volt supply

and was regulated by means of a resistance frame of a maximum resistance of 50 ohms which was immersed in oil and kept cool by an external water-bath.

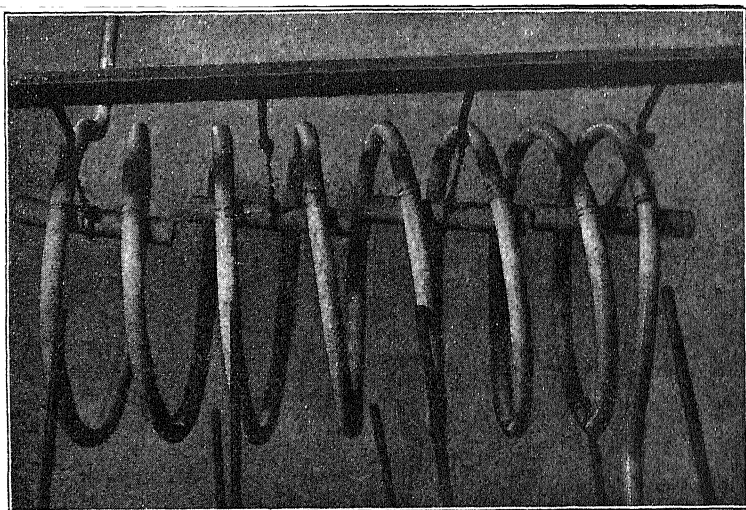


FIG. A.—Wound silica tube, showing method of suspension before kieselguhr was packed round it.

For temperatures below  $450^{\circ}\text{C}$ ., the connections were so arranged that there were four circuits in parallel, each circuit containing four lengths of platinum in series. For higher temperatures eight circuits in parallel were used each with two lengths of platinum in series.

After velocity measurements had been made at ordinary temperatures, the furnace was heated up for several days with a current of 6 ampères which raised the temperature of the coil to about  $230^{\circ}\text{C}$ . Before any measurements were made the current was cut off to allow time for the platinum circuits to cool down to the temperature of the coil. The resistance of the sixteen lengths of platinum were then rapidly measured by means of a post-office resistance box and galvanometer in series with a sixteen-way switchboard. These measurements showed that the two outer sections of the coil were cooler than the middle sections. The two end circuits only were therefore heated for some time and the furnace allowed to cool before resistance measurements were again made; and this heating and cooling were repeated until all sixteen lengths of platinum were of approximately the same resistance. Velocity experiments were then carried out and at the same time temperature readings were taken with the pyrometer; the temperature readings of the outer and inner parts of the coil were found to agree closely. This method of procedure was adopted for determinations of the velocities of

sound in nitrogen at temperatures up to 905° C., for methane and carbon dioxide up to 640° C., and for air at 630° C.

The corrections to be applied for the cooler ends of the tube were determined from distance-temperature curves constructed from measurements of temperature at different distances from the ends.

For example, it was found that at one end of the silica tube the full temperature of the furnace (viz., 800° C.) was reached in 25 cm. inwards from the iron wall of the case, and at the other end the full temperature was reached in 23 cm.; thus over a distance of 48 cm. the temperature varied from 20° to 800°. Outside the furnace wall the sound wave had to traverse a total length of 25 cm. kept water cooled at 20°. It was assumed that the sound traversed the cooled portion (25 cm.) at the velocity already determined at 20°, and over the unequally heated 48 cm. at a velocity corresponding to the mean temperature of this portion of the tube, viz., 410°. The values so corrected probably differ from the true velocities by amounts well within the experimental error.

It was assumed that a similar correction was applicable at all temperatures, the actual correction being of course much less at lower temperatures.

In the following Table are given the mean velocities of sound (corrected as above) determined in the silica tube at the temperatures recorded by the resistance thermometers:—

Table IV.—Silica Tube.

Nitrogen.		Carbon dioxide.		Methane.		Air.	
Tem- perature.	Velocity.	Tem- perature.	Velocity.	Tem- perature.	Velocity.	Tem- perature.	Velocity.
° C.	<i>m/s.</i>	° C.	<i>m/s.</i>	° C.	<i>m/s.</i>	° C.	<i>m/s.</i>
18	344·9	18	264·5	15	433·1		
176·5	426·1	196	332·1	194	529·2		
344	502·0	385·4	386·5	390·4	615·1		
365	513·0	632	445·0	640	711·4	630	585·0
539	557·6	634	447·5				
635	596·3						
905	672·5						

After a number of satisfactory results had been obtained for nitrogen, it was decided that determination of the velocity of sound in this gas could conveniently be used as a means of measuring the temperature of the coil.

It was found when a temperature equilibrium had been reached by prolonged heating, that separate charges of nitrogen gave closely concordant results provided both measurements were made within a short time. It was

easy, therefore, to fill the coil with another gas and measure the velocity of sound in it between two measurements in nitrogen and be assured that the conditions had not altered appreciably. For instance, on January 15, 1914, after the temperature of the silica tube, as measured by the resistance thermometers, had become constant, the mean of five closely concordant determinations gave the velocity of sound in nitrogen as 519.1 m.p.s. The velocity in the free gas calculated from this is 529.9 m.p.s. and the calculated temperature is  $405.4^{\circ}$ . The nitrogen was then swept out by carbon dioxide and the mean of seven closely concordant determinations gave the velocity of sound in carbon dioxide as 395.3 m.p.s. On recharging the tube with nitrogen a new set of five determinations gave the velocity of sound in nitrogen as 519.4 m.p.s., from which the velocity in the free gas is calculated as 530.2 m.p.s. and the temperature as  $406.1^{\circ}$ . A similar set of determinations of the velocity of sound in air made immediately afterwards gave 510.9 m.p.s., from which the velocity in free air is calculated as 521.5 m.p.s. and the temperature  $406.3^{\circ}$ . It is evident that the conditions had remained practically constant during these experiments, and moreover the values for carbon dioxide so found at different temperatures agreed with those where the temperatures were directly measured. This method was adopted for carbon dioxide and air at  $406^{\circ}$  and  $493^{\circ}$  C. with the following results:—

Table V.—Temperatures Calculated from Velocities in Nitrogen.

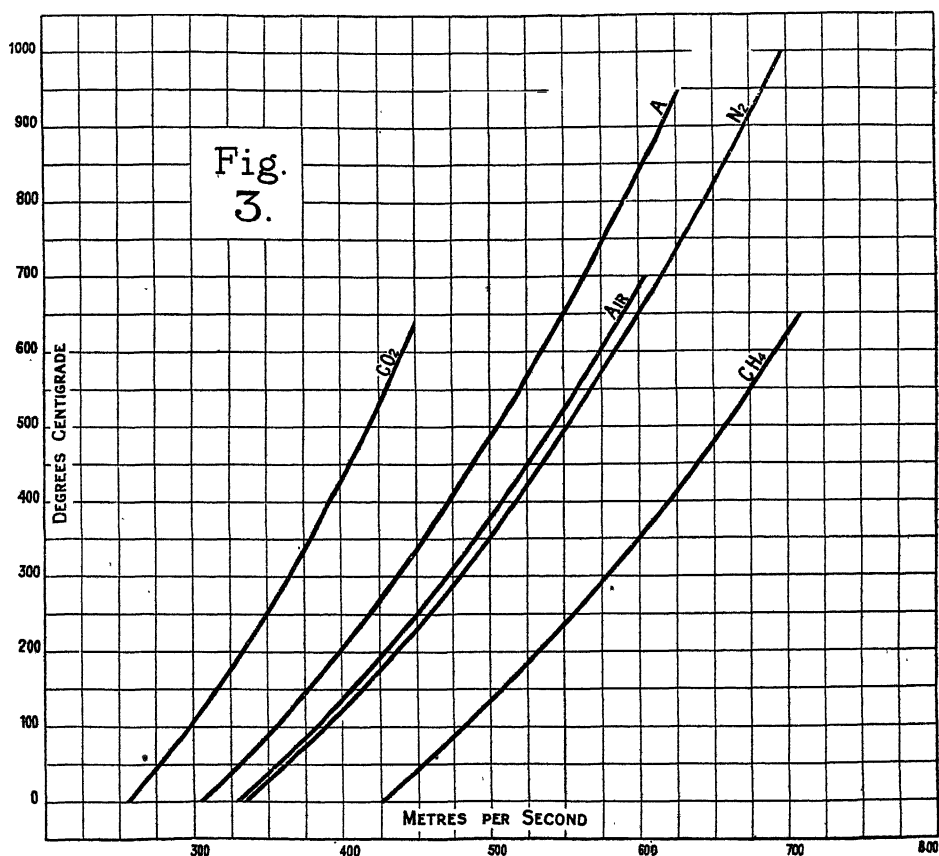
Carbon dioxide.		Air.	
Temperature.	Velocity.	Temperature.	Velocity.
$^{\circ}$ C.	<i>m/s.</i>	$^{\circ}$ C.	<i>m/s.</i>
405.8	395.3	406.3	510.9
493	417.3	492.7	540.8

Similarly by using argon as the standard gas between determinations of nitrogen and of carbon dioxide, and assuming the value of  $\gamma$  for argon to remain constant at 1.667, velocity determinations were made from which the average temperatures of the coil were calculated after applying the necessary corrections. The following results were thus obtained:—

Table VI.—Temperatures Calculated from Velocities in Argon.

Nitrogen.		Carbon dioxide.	
Temperature.	Velocity.	Temperature.	Velocity.
° C.	m/s.	° C.	m/s.
93.5	386.2	94.1	296.0
95.7	387.4		
522.6	559.1		

The results given in Tables I to VI together with the calculated velocities of sound in argon in the silica tube were then plotted graphically, and curves constructed. From these curves (reproduced on a small scale in fig. 3) the values given in Table VII were read off.



Mean velocities of sound in lead, steel, and silica tubes.



Table VII.—Mean Velocities of Sound in Lead, Steel, and Silica Tubes.

Temperature.	Nitrogen.	Argon (calculated).	Air.	Carbon dioxide.	Methane.
° C.	<i>m/s.</i>	<i>m/s.</i>	<i>m/s.</i>	<i>m/s.</i>	<i>m/s.</i>
0	334·4	305·4	328·6	256·6	425·2
100	389·1	355·5	382·5	297·9	481·8
200	436·4	399·0	429·2	333·4	532·5
300	478·6	437·8	470·5	364·7	577·9
400	516·8	472·9	508·1	392·9	618·9
500	551·8	505·5	542·6	419·1	657·2
600	584·3	535·5	574·6	443·0	692·6
700	615·1	563·8	604·6		
800	643·7	590·4			
900	671·0	615·8			
1000	696·8	640·0			

*Relation between Velocities of Sound in Tubes and in "Free Gas."*

The speed of propagation of sound waves has been found to be smaller in gases contained in narrow tubes than in the open. The observed lowering of velocity is caused partly by the heat exchange between the walls of the tube and the compressed or expanded gas, and partly by friction. Before values of  $\gamma$  can be deduced, the velocities of sound measured in tubes must, therefore, be corrected to velocities in the free gases. The problem has been worked out theoretically by Helmholtz and by Kirchhoff,\* who obtained similar mathematical expressions; the only difference consisting in the significance attaching to one of the constants. Both Helmholtz and Kirchhoff represented the velocity of sound in pipes by the expression

$$V' = V [1 - c/2r\sqrt{(\pi N)}], \quad (1)$$

in which  $V$  is the speed in the free gas and  $V'$  is the velocity of sound of frequency  $N$  in a pipe of radius,  $r$ . According to Helmholtz the constant,  $c$ , is the viscosity of the gas, but according to Kirchhoff  $c$  also depends upon the heat exchange between the gas and the wall of the tube and is represented by the expression

$$c = \sqrt{(\mu)} + (V/b - b/V) \sqrt{(\alpha)}, \quad (2)$$

in which  $V$  is the velocity of sound in the free gas and  $b$  is the Newtonian velocity.  $\mu$  and  $\alpha$  are given by the expressions,

$$\mu = \eta/\rho, \quad \text{and} \quad \alpha = k/\rho c_v,$$

where  $\eta$  is the coefficient of viscosity,  $k$  the coefficient of conductivity,  $\rho$  the density of the gas and  $c_v$  the specific heat at constant volume. Substituting the above values of  $\mu$  and  $\alpha$  in (2),

$$c = \sqrt{(\eta/\rho)} + \sqrt{(k/\rho c_v)} (V/b - b/V).$$

\* 'Pogg. Ann.,' vol. 134, p. 177 (1868).

Substituting  $k = 1.6027 \eta_{v,*}$  then

$$c = \sqrt{(\eta/\rho)} [1 + \sqrt{(1.6027) (V/b - b/V)}] \text{ but } V/b = \sqrt{(C_p/C_v)} = \sqrt{(\gamma)},$$

so that 
$$c = \sqrt{(\eta/\rho)} \{1 + \sqrt{(1.6027) [(\gamma-1)/\sqrt{(\gamma)}]}\}. \quad (3)$$

This expression may be used to calculate the variation of  $c$  with temperature for any given gas. According to Sutherland,<sup>†</sup> the variation of the viscosity of a gas with temperature is represented by the expression

$$\eta_t = \eta_0 \frac{1 + C_1/273}{1 + C_1/T} \sqrt{(1 + t/273)}, \quad * (4)$$

where  $C_1$  is a constant for the particular gas under consideration,  $t$  the temperature in degrees centigrade, and  $T$  the temperature on the absolute scale. Considering the case of a perfect gas,

$$\rho_t = \rho_0 \cdot 273/T,$$

so that by substitution in (3)

$$c = \sqrt{\left( \frac{\eta_0 T (1 + C_1/273) \sqrt{(1 + t/273)}}{\rho_0 \times 273 (1 + C_1/T)} \right) \{1 + \sqrt{(1.6027) [(\gamma-1)/\sqrt{(\gamma)}]}\}}. \quad (5)$$

Several investigations have been carried out with the object of testing the validity of the Kirchhoff expression (1). Schneebeil<sup>‡</sup> and Seebech<sup>§</sup> obtained values supporting the Helmholtz and Kirchhoff theories as to the variation of velocity with the diameter of the pipe, but their results were not in agreement with the theoretical dependence of velocity on the frequency of the note employed. From experiments carried out by the method of dust figures in tubes varying in diameter from 25 mm. to 80 mm., Kaiser concluded that the velocity of sound varied with the pitch of the note and the diameter of the pipe, according to the Kirchhoff expression, provided that a higher value than the theoretical be assigned to the constant,  $c$ . It is to be observed that Kirchhoff himself had pointed out that the value of  $c$  would be greater than theoretical if the surface of the tube were not perfectly smooth. Blaikley,<sup>||</sup> using brass organ pipes of a special shape, obtained results which supported the theory with regard to the effect of the frequency of the note and the diameter of the pipe. On the other hand, Müller<sup>¶</sup> and Schulze came to the conclusion that the Kirchhoff expression had no general validity and that the velocity in tubes depends on the material.

\* O. E. Meyer, 'The Kinetic Theory of Gases.'

† 'Phil. Mag.,' vol. 36, p. 507 (1893).

‡ 'Pogg. Ann.,' vol. 136, p. 296 (1869).

§ 'Pogg. Ann.,' vol. 139, p. 104 (1870).

|| 'Phil. Mag.,' vol. 16, p. 447 (1883); p. 328 (1884).

¶ 'Ann. d. Physik,' vol. 2, p. 331 (1903).

From the results of the above-mentioned investigations, it may be concluded that the dependence of velocity on diameter, but not on the frequency of the note employed, is represented by the Kirchhoff formula. The constant is found to be greater than the theoretical value of  $c$ , its exact value varying with the material of the tube.

In the experiments described in this paper, the same note was used for experiments in the same tube and the results in the different tubes were in close agreement. For these experiments the expression

$$V' = V[1 - c/2r\sqrt{(\pi N)}]$$

may therefore be simplified to

$$V' = V(1 - Kc), \quad (6)$$

in which  $K$  is a constant embodying the effect of the frequency of the note, the diameter, material, and shape of the tubes. The theoretical constant,  $c$ , varies with the gas used and the temperature according to equation (5). If the value of  $Kc$  be known for one gas at a given temperature, then its magnitude may be calculated for any other gas at any other temperature. The following values of the Kirchhoff constant,  $c$ , for nitrogen, argon, air, and carbon dioxide at different temperatures have been calculated from equation (5).

Table VIII.

Gas.	Nitrogen.	Argon.	Air.	Carbon dioxide.
$\rho_0 \times 10^3$	1.2507	1.7809	1.2928	1.9768
$\eta_0 \times 10^4$	1.674	2.10	1.733	1.414
Sutherland constant $C_1$	109	160	119.4	277
Temperature, ° C.	Kirchhoff constant, $c$ .			
0	0.52	0.57	0.52	0.36
100	0.69	0.76	0.69	0.48
200	0.84	0.93	0.84	0.59
300	0.99	1.10	0.99	0.69
400	1.12	1.26	1.13	0.79
500	1.26	1.42	1.27	0.88
600	1.38	1.57	1.39	0.97
700	1.51	1.72	1.52	
800	1.62	1.86		
900	1.74	2.00		
1000	1.85	2.13		

Since the Sutherland constant has not been determined for methane, the values of the Kirchhoff constant,  $c$ , for this gas at different temperatures

have been calculated from the simpler expression of O. E. Meyer and v. Obermeyer.

$$\eta_t = \eta_0 (1 + \beta t).$$

In the case of ethane, the viscosities have been assumed to be  $1.03 \times 10^{-4}$  at  $10^\circ \text{C}$ .,  $1.15 \times 10^{-4}$  at  $50^\circ \text{C}$ ., and  $1.30 \times 10^{-4}$  at  $100^\circ \text{C}$ .

Table IX.

Methane.	
$\rho_0 \times 10^3$	0.7171
$\eta_0 \times 10^4$	1.040
$\beta$	0.003
Temperature, $^\circ \text{C}$ .	Kirchhoff constant, $c$ .
0	0.51
100	0.64
200	0.78
300	0.91
400	1.04
500	1.17
600	1.30
Ethane.	
$\rho_0 \times 10^3$	1.3906
Temperature, $^\circ \text{C}$ .	Kirchhoff constant, $c$ .
10	0.34
50	0.38
100	0.44

Recent determinations of the velocity of sound in free nitrogen, and calculations from accepted values of  $\gamma$ , lead to the conclusion that the velocity of sound in free nitrogen at  $0^\circ \text{C}$ . is probably 337.5 metres per second. Substituting this value of the velocity and the calculated Kirchhoff constant, 0.52, in equation (6), the constant K for the tubes used is found to be practically the same for the three tubes, viz., 0.018.

Equation (6) then becomes

$$V' = V(1 - 0.018c).$$

From this expression the velocities of sound given in Table VII have been corrected to velocities in the free gases, and the following results obtained (Table X):—

Table X.

Temperature.	Velocities of sound in free gas in metres per second.				
	Nitrogen.	Argon (calculated).	Air.	Carbon dioxide.	Methane.
° C.					
0	337·5	308·5	331·8	258·3	429·2
100	394·1	360·3	387·5	300·4	487·4
200	443·1	405·7	435·8	336·9	540·0
300	487·2	446·5	479·0	369·3	587·3
400	527·3	483·9	518·6	398·6	630·8
500	564·5	518·6	555·2	425·7	671·4
600	599·4	551·1	589·3	450·9	709·2
700	632·2	581·7	621·6		
800	663·0	610·9			
900	692·4	638·7			
1000	720·6	665·5			
				Temp., ° C.	Ethane.
				10	307·7
				50	327·4
				100	349·3

The relationship existing between the molecular heat values of a gas at constant pressure and constant volume are expressed in the two following equations, developed by E. Warburg from Berthelot's equation of state :—\*

$$(a) \quad C_p - C_v = R(1 + \pi \cdot 9/128 \cdot 24\tau^3),$$

$$(b) \quad C_p/C_v = \frac{V^2 M}{RT} [1 - \pi \cdot 9/128 \cdot 2\tau(1 - 6\tau^2)],$$

in which  $\pi = p/p_x$ ,  $p$  = pressure,  $p_x$  = critical pressure;  $\tau = T_x/T$ ,  $T$  = temperature (absolute),  $T_x$  = critical temperature (absolute);  $R$  in (a) = 1·985 and (b) =  $82 \cdot 07 \times 1033 \cdot 3 \times 981 \cdot 183$ ;  $V$  is the velocity of sound in centimetres per second and  $M$  is the molecular weight of the gas.

From the two equations (a) and (b), and the velocities of sound given in Table X, the molecular heats of the gases under consideration have been calculated in Tables XI to XV.

It is obvious that the specific heats of nitrogen and of air rise fairly regularly with the temperature, the values for equal increments of temperature falling nearly on a straight line between 0° and 700°. Between 700° and 1000° the values found for nitrogen are more irregular, as might be expected, the value at 800° being probably too high and that at 1000° too low. In Table XII the values of  $C_v$  for nitrogen are calculated from the expression :—

$$C_v = 4 \cdot 82 + 0 \cdot 00024T + 0 \cdot 00000013T^2.$$

\* Nernst, 'Theoretische Chemie,' 7. Aufl., s. 245.

Table XI.—Nitrogen.

Temperature.	M = 28·02.	$p_x = 33 \cdot 0$ .	$T_x = 127$ .	C <sub>v</sub> calculated from 4·775 + 0·00042T.
	C <sub>p</sub> - C <sub>v</sub> .	C <sub>p</sub> /C <sub>v</sub> .	C <sub>v</sub> .	
° C.				
0	1·9952	1·408	4·890	4·890
100	1·9900	1·404	4·926	4·932
200	1·9870	1·400	4·968	4·974
300	1·9862	1·396	5·014	5·016
400	1·9857	1·392	5·066	5·058
500	1·9855	1·389	5·104	5·100
600	1·9853	1·386	5·143	5·142
700	1·9853	1·383	5·184	5·184
800	1·9852	1·379	5·238	5·226
900	1·9851	1·376	5·280	5·268
1000	1·9850	1·374	5·308	5·310

Table XII.

Temperature.	C <sub>v</sub> found.	C <sub>v</sub> (calculated).
° C.		
0	4·890	4·896
100	4·926	4·928
200	4·968	4·963
300	5·014	5·001
400	5·066	5·041
500	5·104	5·084
600	5·143	5·129
700	5·184	5·177
800	5·238	5·228
900	5·280	5·280
1000	5·308	5·336

The values deduced from our experiments on nitrogen are lower than those calculated by Bjerrum and those recently given by Tizard and Pye.\*

Table XIII.—Carbon Dioxide.

Temperature.	M = 44·005.	$p_x = 73 \cdot 0$ .	$T_x = 304$ .	C <sub>v</sub> calculated from 6·1 + 0·0028T.	C <sub>v</sub> calculated from 6·30 + 0·00205T + 0·0000007T <sup>2</sup> .
	C <sub>p</sub> - C <sub>v</sub> .	C <sub>p</sub> /C <sub>v</sub> .	C <sub>v</sub> .		
° C.					
0	2·0484	1·296	6·920	6·864	6·912
100	2·0098	1·281	7·152	7·144	7·160
200	1·9972	1·270	7·397	7·424	7·427
300	1·9919	1·260	7·658	7·704	7·705
400	1·9892	1·249	7·989	7·984	7·997
500	1·9878	1·240	8·282	8·264	8·303
600	1·9870	1·230	8·639	8·544	8·623

\* 'Automobile Eng.,' February and March, 1921.

The variation of  $C_v$  with temperature for carbon dioxide may therefore be represented approximately by the expression

$$C_v = 6.1 + 0.0028T,$$

or, more accurately, by the expression,

$$C_v = 6.30 + 0.00205T + 0.0000007T^2.$$

The values found by us for carbon dioxide are also lower than those calculated by Bjerrum and by Tizard and Pye.

Table XIV.—Methane.

Temperature.	$M = 16.037.$	$p_x = 50.0.$	$T_x = 177.5.$	$C_v$ calculated from $6.66 + 0.019t.$
	$C_p - C_v.$	$C_p/C_v.$	$C_v.$	
° C.				
0	2.0034	1.301	6.656	6.66
100	1.9922	1.228	8.738	8.56
200	1.9885	1.188	10.577	10.46
300	1.9870	1.160	12.419	12.36
400	1.9862	1.139	14.288	14.26
500	1.9858	1.124	16.015	16.16
600	1.9856	1.111	17.883	18.06

The above results, which show a rapid increase in the value  $C_v$  with rise of temperature for methane over the range experimented on, may be represented approximately by the equation

$$C_v = 6.66 + 0.019t \text{ at } t^\circ \text{ Centigrade.}$$

It is to be noted that methane begins to decompose, giving hydrogen and carbon, at a temperature of  $700^\circ \text{C.}$  in a silica tube.

Table XV.—Ethane.

Temperature.	$M = 30.058.$	$p_x = 50.2.$	$T_x = 307.$
	$C_p - C_v.$	$C_p/C_v.$	$C_v.$
° C.			
10	2.0685	1.224	9.22
50	2.0420	1.208	9.82
100	2.0222	1.186	10.87

The values of  $C_v$  for ethane between  $10^\circ$  and  $100^\circ$  may therefore be represented by the expression

$$C_v = 9.04 + 0.0183t \text{ at } t^\circ \text{C.}$$

The expressions representing the molecular heats at constant volume and different temperatures of the gases considered in this paper are grouped

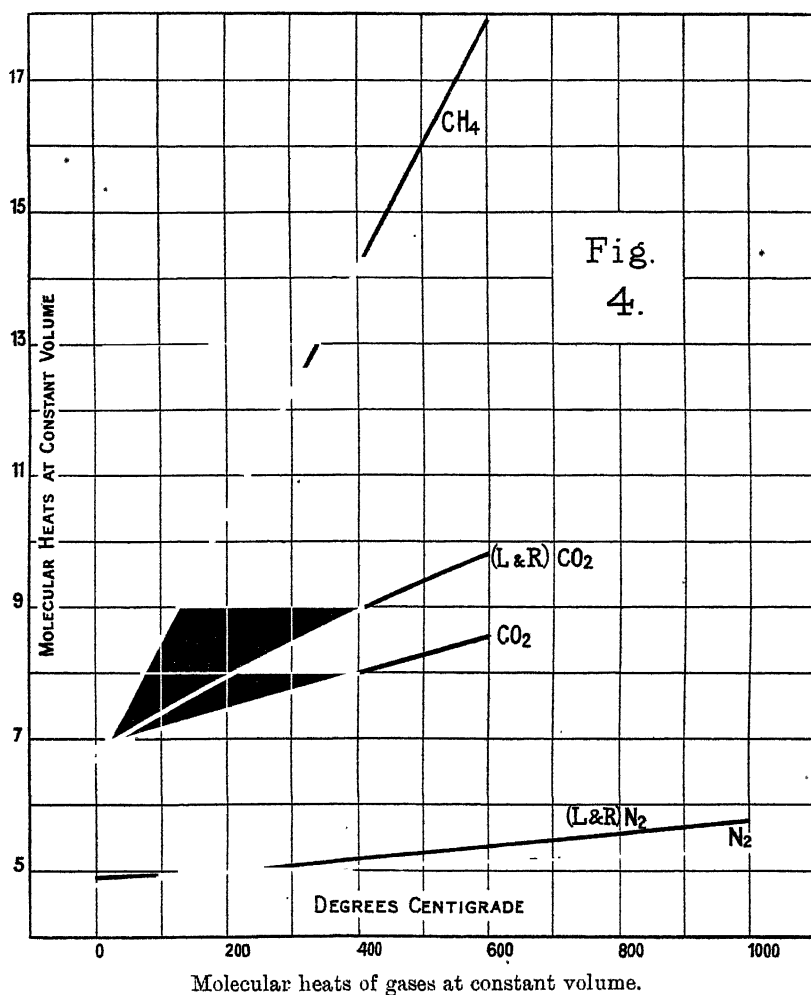


Table XVI.—Variation of  $C_v$  with Temperature at  $T^\circ$  abs. or  $t^\circ$  C.

Gas.	Temperature range.	$C_v$ .	$C_v$ (Lewis and Randall).
Nitrogen .....	$^\circ$ C. 0-1000	$4.775 + 0.00042 T$	$4.5 + 0.001 T$
Air .....	0-700	$4.8 + 0.0004 T$	$4.5 + 0.001 T$
Carbon dioxide .....	0-600	$6.30 + 0.00205 T$ $+ 0.0000007 T^2$	$5.0 + 0.0071 T$ $- 0.00000186 T^2$
Methane .....	0-600	$6.66 + 0.019 t$	
Ethane.....	0-100	$9.04 + 0.0183 t$	



together in Table XVI and compared with those deduced by Lewis and Randall.\* They are also shown graphically in fig. 4 (p. 25).

Previous determinations of  $C_p/C_v$  for methane at approximately 20° C. by Mason,† Müller,‡ and Capstick§ give a mean value of 1.313, which is rather higher than that obtained from the experiments described in this paper; although Lussana|| obtained a value of 9.464 for  $C_p$  from 0° C. to 100° C., which is in good agreement with the authors' figure of 9.606.

In the case of ethane, Daniell and Pierron¶ and Capstick\*\* obtained values of 1.22 and 1.182 respectively for the ratio of the two specific heats at ordinary temperature, as against the authors' value of 1.221 at 15° C.

We have to thank those research students who gave us assistance during the earlier stages of this investigation, and in particular Messrs. W. H. Bentley, D.Sc., F. Fairbrother, M.Sc., and H. Henstock, Ph.D.

The authors regret the unavoidable delay—due to the war—in presenting the results of these experiments, most of which were carried out during the years 1912 to 1915. They wish to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for a grant towards the expense of the apparatus employed, and to the Council of the Chemical Society for a grant towards the cost of the chemicals used.

\* 'Journ. Amer. Chem. Soc.,' vol. 34, p. 1128 (1912).

† 'Ann. Chim. Phys.' [3], vol. 53, p. 277 (1858).

‡ Müller, 'Wied. Ann.,' vol. 18, p. 95 (1883).

§ 'Roy. Soc. Proc.,' vol. 54, p. 101 (1893).

|| 'Nuovo Cimento' [3], vol. 5, pp. 70, 130 (1896); vol. 7, pp. 61, 365 (1898).

¶ 'Bull. Soc. Chim.' [3], vol. 21, p. 801 (1899).

\*\* 'Roy. Soc. Proc.,' vol. 54, p. 101 (1893).

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*The Ratio of the Specific Heats of Air and of Carbon Dioxide.*

By J. R. PARTINGTON, D.Sc.

(Communicated by Dr. J. A. Harker, F.R.S. Received May 26, 1921.)

Although our knowledge of the energy-content of solid bodies has been greatly extended by the theoretical investigations of Planck, Einstein and Debye, and by the experiments of Dewar, Nernst and others, the problem in the cases of gases, and especially of vapours, is still far from a satisfactory solution. With the object of providing accurate data for a theoretical study of the energy-content of molecules in gases, the experiments described in this paper were commenced in 1911 in the laboratory of the Physikalisch-Chemisches Institut of the University of Berlin. I desire to express my thanks to Prof. Nernst for the interest he showed in this work, and for many useful suggestions he made during the period 1911–1913, in which I worked in his laboratory.

Since air and carbon dioxide have been the object of some very careful investigations by previous experimenters, it was decided that a re-investigation of the ratio of the specific heats,  $c_p/c_v$ , of these gases would be appropriate at the commencement of the research. Other gases, for which the constants are less accurately known, such as ammonia, sulphur dioxide, nitrous oxide and nitrogen, are at present under investigation by a method similar to that described in the present communication. The present results were published in an abstracted form in 1913.\*

The first measurements of the ratio of the specific heats of air were made by Clément and Desormes in 1812. A vessel filled with air at a pressure  $p_1$ , slightly greater than atmospheric, is put in communication with the free air at pressure  $P$ , by opening a stopcock, so as to equalise the pressures in the sudden, nearly adiabatic, expansion. The stopcock is then rapidly closed, and the air in the vessel allowed to regain its initial temperature. The pressure  $p_2$  is then determined. If  $\gamma = c_p/c_v$  is the ratio of the specific heats, then (i) if the gas is ideal ( $pv = RT$ ); (ii) if the specific heat at constant volume,  $c_v$ , is independent of temperature over the range used in the experiment, it is readily shown that

$$\gamma = \frac{\log p_1 - \log P}{\log p_1 - \log p_2}. \quad (1)$$

One source of error in this method is the exchange of heat between the gas and the walls of the vessel during the expansion. This is greater the

\* 'Physikalische Zeitschrift,' vol. 14, p. 969 (1913).

larger the ratio of the surface to the volume of the vessel used to contain the gas. Roentgen,\* using a 7-litre cylinder, obtained values of  $\gamma$  for air not greater than 1.29, although he attempted to correct for heat exchange between the gas and the vessel. With a 70-litre globe he obtained a value of  $\gamma$  of 1.405. Another source of error was brought to notice by Cazin,† viz., the oscillations of pressure when the stopcock is opened. The kinetic energy of the outrushing gas may lead to a diminution of pressure in the globe below atmospheric pressure. This is followed by a back-rush of air, which again may overshoot the equilibrium pressure. It is practically impossible to close the stopcock at exactly the right moment of equalisation of pressure, and, if attempts are made to prevent the surging of the gas by the use of a narrow outlet, the extended time of outflow leads to serious error, by reason of heat exchange between the gas and the walls of the vessel.

Roentgen avoided these difficulties by using a 70-litre globe, in which the heat exchange was diminished, and by closing the stopcock before equalisation of pressure was attained. The pressure was determined by a metallic membrane manometer, communicating with the gas through a hole in the side of the vessel. The effects of heat exchange were determined by taking a series of manometer readings as the gas warmed up after the expansion. Since the German-silver membrane showed a slight lag ("elastische Nachwirkung"), a somewhat complicated correction for this was necessary. The mean of the experiments with air gave  $\gamma = 1.4053$ , and with carbon dioxide  $\gamma = 1.3052$ . The effect of the walls was studied by inserting glass tubes into the globe until the ratio of surface to volume rose from 0.0834 to 0.1600. The value of  $\gamma$  for air was reduced from 1.4037 to 1.3912. The values of Roentgen (with the exception of that for hydrogen, which he recognised as too low, on account of the large thermal conductivity of the gas) were much more accurate than any previous determinations. There is little doubt, however, that they are affected by a constant error of about 0.15 per cent.

F. Kohlrausch‡ attempted to measure the changes of temperature produced in adiabatic expansion. Favre and Silbermann had previously made some experiments with a Breguet metal thermometer in air, which was suddenly rarefied by a pump, but they found only about one-tenth of the theoretical fall in temperature. This result they attributed to the lag of the thermometer. Kohlrausch, using a 6-litre vessel, attempted to correct for heat exchange

\* 'Annalen der Physik,' vol. 141, p. 552 (1870); vol. 148, p. 580 (1873).

† 'Phil. Mag.,' vol. 40, pp. 81, 197, 268 (1870).

‡ 'Annalen der Physik,' vol. 136, p. 618 (1869).

with the walls by taking readings after the expansion and using Newton's law of cooling. He was unable to obtain higher values for air than  $\gamma = 1.302$ . The very serious effect of heat exchange with the walls was at that time not appreciated.

An appreciable step in advance was the substitution of a thin wire resistance thermometer for the massive metal thermometer. Lummer and Pringsheim\* used a spiral of fine silver wire at the centre of a 70-litre globe. The low value of  $\gamma = 1.384$  obtained for air, these experimenters assumed to be due to the lag of the thermometer and to heat conduction from the leads. In the method in which the temperature after expansion is measured, the error caused by oscillation of gas on opening the stopcock may be largely eliminated, since it is not necessary to close the stopcock again after the expansion has occurred. If  $T_1$  and  $T_2$  are the absolute temperatures of the gas before and after adiabatic expansion, then it can be shown, with the same assumptions as were introduced in the deduction of (1), that

$$\gamma = \frac{\log p_1 - \log P}{(\log p_1 - \log P) - (\log T_1 - \log T_2)} \quad (2)$$

In a later set of experiments, Lummer and Pringsheim† used a platinum strip bolometer, constructed by rolling out a silvered platinum wire ("Wollaston wire"), and dissolving in nitric acid the silver from the central portion, so as to leave exposed a strip of platinum, 7 cm. long, 0.2 cm. wide, and 0.0006 mm. thick, extending through a silvered part, 0.0066 mm. thick and 0.2 cm. wide, to the thicker silver leads, which were soldered to thick copper leading wires. This thin strip was supported so as to hang freely downwards in the form of a loop in the centre of a 90-litre spherical globe of copper fixed in a water bath. The pressure was read on a sulphuric acid manometer to 0.2 mm. The resistance of the bolometer was balanced on a Wheatstone's bridge, a specially constructed Thomson galvanometer, with a short period of 4 seconds, being used as a null instrument. The initial pressure  $p_1$  was varied until, after the resistance in the bridge had been lowered by an arbitrary amount, there was no deflection when the galvanometer was put in circuit immediately after the expansion. The temperature of the gas before expansion was that of the water bath, which was measured to 0.01° C. by means of a mercury thermometer. The temperature after expansion was ascertained by adding iced water to the bath until the resistance of the bolometer was reduced to the value observed after the expansion. The temperature of the water was then taken as before.

\* 'British Association Reports,' p. 565 (1894).

† 'Annalen der Physik,' vol. 64, p. 553 (1898).

The systematic errors in the method of Lummer and Pringsheim may now be briefly considered, since the method adopted in the research now described was a modification of the former method, in which the errors were either altogether eliminated or brought more under control. The systematic errors in Lummer and Pringsheim's experiments they stated to be as follows:—

(1) The acquisition of heat by the bolometer by conduction from the gas and along the leads from the warmer thick leads and the walls of the vessel.

(2) Convection currents rising from the lower warmer walls and ascending through the gas. Convection from the leads themselves would, owing to the position of the loop below them, have no effect.

(3) The direct heating of the bolometer owing to absorption of radiation from the warmer walls of the vessel.

To these may be added a fourth source of error, which does not seem to have been adequately considered by Lummer and Pringsheim, viz. :—

(4) The uncertainty introduced into the temperature measurements by the lag of the bolometer, and particularly by the period of the galvanometer.

The effects of conduction and convection from the walls through the gas Lummer and Pringsheim considered were eliminated by the position of the bolometer in the centre of a large mass of gas. In support of this they found the same change of resistance with variation of the time of expansion from 2 to 8 seconds. The resistance also remained constant for several seconds after the expansion. It is evident, however, that the fourth possible source of error might vitiate the soundness of this conclusion, because a stationary state may be attained which does not correspond with the minimum temperature after expansion. The thick leads remain for an appreciable time at or near the initial temperature, whereas the central part of the bolometer, with its very small thermal capacity, rapidly assumes a temperature very near that of the colder surrounding gas. There will be a gradient of temperature from the leads to the thin strip, which becomes less and less steep as the leads cool down. Superposed on this effect, however, is the gradual rise in temperature of the gas surrounding the whole bolometer system, which is very approximately followed by the temperature of the thin strip. (The effects produced by convection appear only several seconds later.) The parts of the thin strip in the vicinity of the junction with the leads have initially a higher temperature than the central portions, but this difference, owing to the reasons just described, will gradually diminish whilst all the time the temperature of the whole metal system is rising. It is obvious without detailed calculation that, with the arrangement adopted by Lummer and Pringsheim, the resistance of the bolometer will pass through a minimum value shortly after the expansion,

and will then steadily rise until the strong convection currents rising through the gas impinge on the bolometer, the resistance of which then becomes very irregular.

The correctness of this criticism was shown experimentally at the commencement of the present research. A single platinum wire 0.001 mm. diameter was suspended at the centre of a 35-litre globe by thicker silver leads, and the changes of resistance after expansion were followed by direct observation with a string galvanometer with a period of about 0.01 second. Immediately after the expansion the throw of the filament in the galvanometer attained a steady position, but this changed slowly in the direction indicating a diminished resistance for about 2 seconds, when the resistance attained a minimum value. After about 6 seconds convection currents caused the resistance to vary considerably.

The calculations of Lummer and Pringsheim led them to the conclusion that the gradient of temperature between the thin strip and the leads was considerably reduced by rolling out the leads in the manner described, but since they assumed that a stationary state was rapidly attained, and since the long period of their galvanometer did not permit of observation of the resistances from the instant of expansion, it is by no means certain how far their results are affected by this source of error.

The inertia of the thin portion of the bolometer to changes of temperature is also a matter of importance. Lummer and Pringsheim ascertained by calculation that with the arrangement used in their experiments the initial difference of temperature between the cold gas and the thin strip was reduced to  $1/e$  of its value in a time of the order of 0.1 second. The same value is found for the wire used in the preliminary experiments just described, and the very rapid attainment of the first position of the deflection confirms the supposition that the inertia of the thin part of the bolometer is small.

A further experiment was made with three wires, of diameters 0.05, 0.01, and 0.001 mm. respectively, in a 35-litre globe. The differences of temperature after equal expansions were determined by the deflections of the string galvanometer. These deflections were, after correction for the previously measured and slightly different temperature coefficients of the wires, in the proportion 351, 372 and 377 respectively. These numbers are in linear relation to the diameters of the wires, as indicated by the theory of heat transfer. The lag with the thick wire could readily be seen, since the movement of the galvanometer filament across the scale after expansion occupied 2 to 3 seconds, whereas with the other two wires the motion was too rapid to follow with the eye. With the thicker wires, of diameter 0.025 mm., used by Makower\* and

\* 'Phil. Mag.,' vol. 5, p. 226 (1903).

by Moody\* there must, therefore, have been an appreciable lag, which would affect the methods of extrapolation used by these experimenters and discussed later in this paper.

The remaining systematic error, due to radiation from the walls of the vessel to the bolometer, was corrected by Lummer and Pringsheim as follows. A blackened platinum wire was substituted for the bright one, and the ratio of the absorbing powers was then known from separate experiments to be 1 to 15 for bright and black wires, respectively. If  $\gamma_1$  and  $\gamma_2$  are two values of  $\gamma$  determined with bright and black wires, respectively, the corrected value is easily shown to be  $\gamma = \gamma_1 + (\gamma_1 - \gamma_2)/14$ . Lummer and Pringsheim found the values  $\gamma_1 = 1.400$  and  $\gamma_2 = 1.370$ , hence the correction for radiation was 0.0021. The final result for air at room temperature was  $\gamma = 1.4025$ .

The method of Lummer and Pringsheim was improved by Makower (*loc. cit.*), who eliminated the uncertainty as to the gradient of temperature at the junctions of the leads and the bolometer itself by making use of the well-known method of compensation of Prof. Callendar. A short piece of the bolometer wire is soldered to an exactly similar pair of leads, placed near the main leads in the gas, and connected in series with the variable resistance arm of the bridge. All changes which occur in the leads are thus exactly compensated by identical changes in the second system, which are compensated in the bridge arrangement. Makower used a 50-litre copper globe, the pressures being measured on a paraffin manometer, which is superior to one filled with sulphuric acid in its permanence, although the viscosity of paraffin makes it rather more difficult to obtain readjustment of levels rapidly. The resistance was measured by a null method, and from it the temperature calculated to  $0.01^\circ \text{C}$ . by Prof. Callendar's formula. A mercury contact automatically closed the bridge circuit after a period,  $t$ , which could be varied and was recorded on a chronograph. Values of  $\gamma$  for different values of  $t$  were found, and the values of  $(\gamma - 1)/\gamma$ , which are proportional to  $T_1 - T_2$ , were plotted against those of  $t$ . By extrapolation to  $t = 0$  it was assumed that the error due to the warming of the gas during the expansion would be eliminated. This assumption does not appear to be entirely satisfactory. The plotted points are somewhat irregularly distributed. For small values of  $t$  the values of  $(\gamma - 1)/\gamma$  are nearly constant; they then fall rapidly until  $t$  is about 2 seconds, remaining constant after this up to about 5 seconds. With the thick wires used (0.025 mm. diameter) there must have been an appreciable lag, which would affect just those measurements with small values of  $t$  most appreciably. It is, therefore, to be expected that Makower's value

\* 'Physical Review,' vol. 34, p. 275 (1912).

of  $\gamma$ , which when corrected for the deviation of air from the ideal state is  $\gamma = 1.402$ , will be a little too small.

In a research by W. H. Moody (*loc. cit.*), which appeared whilst the present experiments were in progress, a thermocouple of copper and constantan wires, 0.025 mm. diameter, was used, one junction being in the external water bath at 25° C. and the other in the centre of a 60-litre globe containing the gas. The E.M.F. was compensated by a potentiometer against a Weston cell, the dependence of the E.M.F. of the thermocouple on the difference of temperatures of the junctions having previously been determined. The temperatures were measured to 0.01° ( $5 \times 10^{-7}$  volt), the effects of conduction along the leads being wholly neglected. To avoid disturbances in the gas, which it was assumed would occur after expansion, the circuit was closed only 2 to 3 seconds after expansion. Experiments with different excess pressures, from 1.2 to 12 cm. of mercury, were made, and the values of  $\gamma$ , plotted against the excess pressure, were extrapolated to zero pressure difference. The radiation correction was found indirectly by comparing the stationary temperatures assumed by the bright and blackened thermocouple in a glass vessel exposed to radiation. Its value was 0.002. Moody made no attempt to correct his results for deviations from the gas laws, even in the case of carbon dioxide. His result for air, so corrected, is  $\gamma = 1.4021$ . It appears to be less accurate than those of Lummer and Pringsheim and of Makower. The thermoelectric method of temperature measurement is less satisfactory than the use of the platinum thermometer, since it is impossible to eliminate the effects of the leads. The assumption of the ideal state for the gases, made by Moody, has also been criticised by Hebb,\* whose value of the velocity of sound was quoted by Moody in support of his value of  $\gamma$ .

The method of Maneuvrier† is less suitable for moderate pressures than for pressures considerably greater than atmospheric. A vessel of 50 litres capacity was connected with a cylindrical tube fitted with a piston. The latter could be forced in to any desired extent by a spring, the duration of the stroke being  $1/12$  to  $1/37$  second. Connected with the globe was a stop-cock, which was automatically opened after the compression and communicated with a U-tube containing water, to the other surface of which any desired static pressure of air could be applied. The latter pressure was adjusted until there was no motion of the water surface when the manoscope was put in communication with the globe after the compression. The pressure change in the adiabatic compression was thus found directly; the corresponding

\* 'Trans. Royal Society of Canada,' vol. 13, sec. 3, p. 101 (1919).

† 'Annales de Chimie et de Physique,' vol. 6, p. 321 (1895); 'Journal de Physique,' vol. 4, pp. 341, 445 (1895).



isothermal change was calculated, allowance being made for deviations from the gas laws, and the ratio  $(\Delta p)_Q/(\Delta p)_T$  is equal to  $\gamma$ . The results of Maneuvrier are readily seen to be affected by two kinds of error. The accuracy of measurement of  $(\Delta p)_Q$  is less with small compressions, whilst the loss of heat during compression is greater with large compressions and with gases of high thermal conductivity. The influence of the two errors is well illustrated by the following results with hydrogen (good conductor) and carbon dioxide (poor conductor) at different compressions:—

Length of piston stroke.	$\gamma$ for CO <sub>2</sub> at 10° C.	$\gamma$ for H <sub>2</sub> .
cm.		
2·5	1·2980	1·4022
5·0	1·2939	1·3850
10·0	1·2983	1·3759
15·0	1·3013	1·3723

It is clearly not correct to take the means of these values. For the reasons given, the value  $\gamma = 1·3013$  for carbon dioxide and 1·4022 for hydrogen may be considered as most probable, although the latter will be slightly too small.

A long series of experiments were made as a preliminary to the present research by a method similar to that of Maneuvrier, since, if accurate results could be obtained by this method, it would be the most suitable for the investigation of gases which are not readily obtained in large quantities in the pure state. Instead of measuring the pressure, however, attempts were made to measure the temperature after compression of air by a piston, by means of thermocouples or bolometers. The temperature observed was always considerably below the correct value.

From the account of previous experiments given above it is clear that a satisfactory method should include the use of:—

(1) A large expansion vessel, to eliminate the effects of conduction and convection in the gas.

(2) A bolometer with as small a heat capacity as possible, practically free from lag and so constructed as to eliminate all effects due to conduction of heat from the leads.

(3) A galvanometer of very rapid period, by means of which the temperature changes in the gas during and after the expansion can be followed in detail, and information thus obtained as to how nearly conditions (1) and (2) have been approached.

The arrangement adopted consisted of a spherical expansion vessel, larger than any previously used, a platinum-wire bolometer, constructed of the

finest obtainable Wollaston wire (0.001 to 0.002 mm. diameter), with compensating leads of the same wire, and an Einthoven string galvanometer, capable of recording changes in the resistance of the bolometer occurring within 0.01 second.

The expansion vessel, A, fig. 1 (see p. 36), consisted of a spherical globe of hammered copper, of 120—130 litres capacity, with two lateral outlets, 10 cm. long and 5 cm. diameter. At the top was a narrow brass pipe for admission of gas. The globe was immersed in a strong cylindrical water bath, B, of tinned iron, covered inside with two coats of white enamel paint. The globe was held firmly in position by having its lateral outlets soldered through holes in the bath, and by a steel cross-bar secured to the top of the bath and pressing in a groove in a circular wooden cap fitting over the top of the globe, the inlet pipe being bent slightly to one side to allow of this. By this means the upward thrust of about 120 kilog. was held in equilibrium. The bath was covered with a wooden lid, having a square trap-door and apertures for stirrers, thermometers, etc. After attempts to use electrical and steam heating, it was found most satisfactory to use gas heating for the bath. The latter was placed on a strong iron-topped table, with part projecting over the edge. This was heated by a powerful three-flame burner, and the water kept stirred by two spiral stirrers placed on opposite sides of the globe and rotated by an electromotor. In this way an initial temperature of about 20° C. could be used, and since the Berlin tap-water had a fairly uniform temperature of about 10° C. the final adjustment of temperature could be attained without having recourse to ice. The work was carried out in a dark basement room with a very uniform temperature of 16° C., which is about the mean of the initial and final temperatures employed.

The expansion occurred through one of the lateral apertures which terminated in a massive brass plate and neck, soldered to, and therefore in good thermal contact with, the water-bath. To the end of this neck was screwed the expansion valve, C. The diameter of the aperture in this valve could be varied by inserting diaphragms of brass plate which were screwed tightly against the carefully machined rim of the neck and caulked with a little red lead and linseed oil. The covering flap of the expansion valve had a circular groove cut in it, in which was cemented a thick flat ring of black vulcanised rubber. The flap was closed over the rim and kept tightly in position by the tooth in the lower lever,  $\alpha$ , engaging in a slot in the steel bar,  $\beta$ , on the lower part of the lid. The seal was perfectly gas-tight. A strong spiral steel spring,  $\gamma$ , between the upper lever,  $\delta$ , and the top of the water-bath provided a means of opening the valve rapidly, so that the flap was cleared of the outward rush of gas and was maintained in this position. A block of wood,

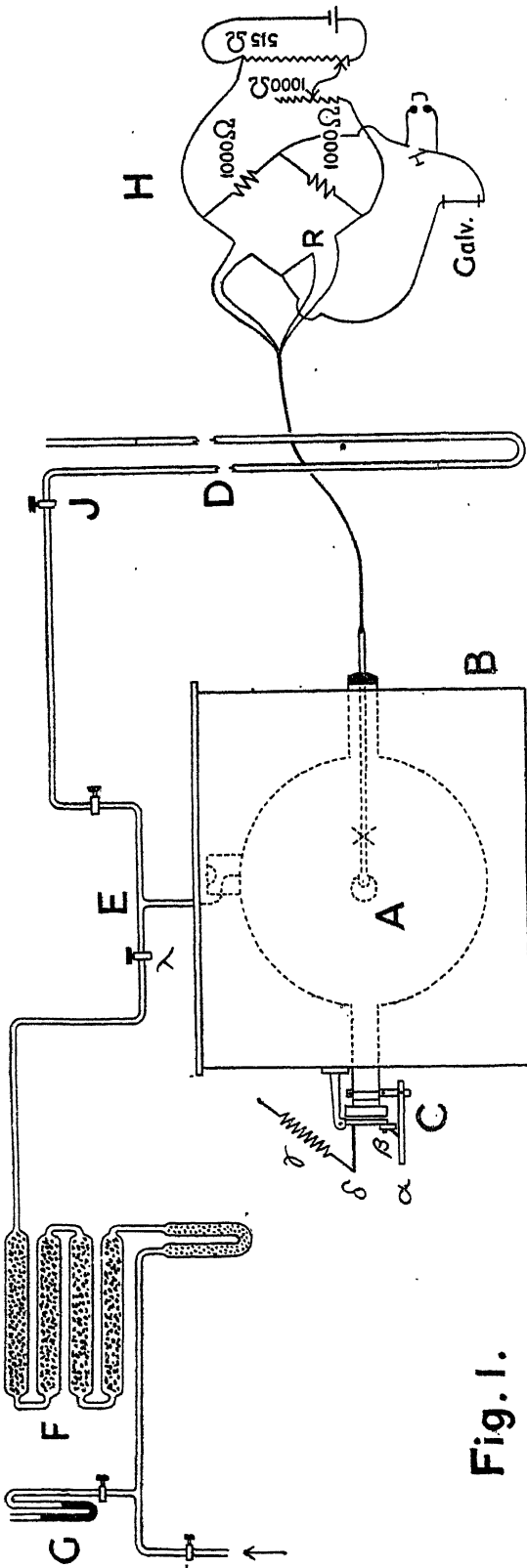


Fig. 1.

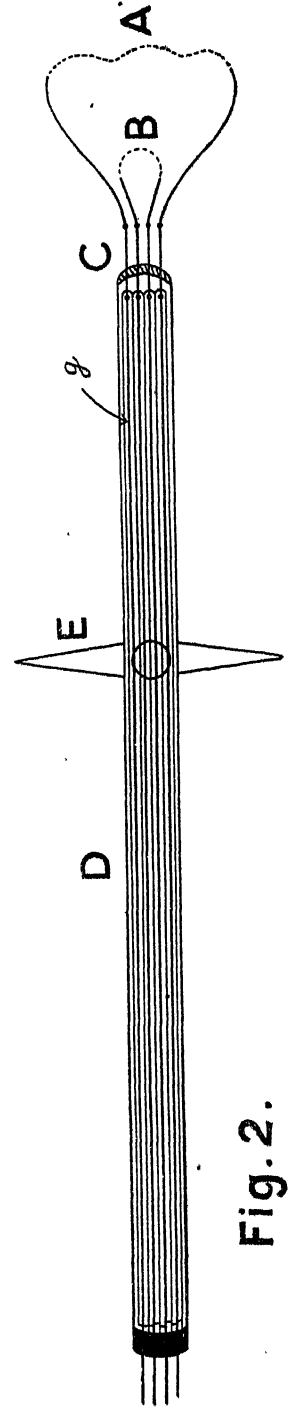


Fig. 2.

clamped in position, received the impact of the upper lever. The correct position of the tooth on  $\alpha$  could be adjusted by making the latter hinge on a split-ring, which was firmly fixed around the valve C by a bolt and nut, and could be adjusted to the required position.

The air used in the experiments was taken from a steel cylinder at 100 atmosphere pressure through a reducing valve and had previously been freed from carbon dioxide and dried in the process of compression. It passed through a soda-lime tube, three long tubes of granular calcium chloride, and a long tube of phosphorus pentoxide, F, on its way to the globe. By means of a small mercury manometer, G, attached to the inlet tube by a T-joint, the approximate pressure required in the globe could be attained without undue disturbance of the levels in the principal manometer, which was filled with pure white paraffin oil. This manometer, D, was then put in connection with the globe for the final adjustment of pressure by opening the large stop-cock, J. A T-joint near the air inlet allowed of air being let out of the globe when necessary through a screw-clip. The stop-cock,  $\lambda$ , near the inlet of the globe was closed after filling the latter with gas.

The principal manometer, D, was a long glass U-tube fixed to a board, with an accurate millimetre scale etched on the glass, and was filled with colourless, anhydrous paraffin oil of high boiling-point, the density of which at  $t^{\circ}\text{C.}$  was found to be  $d_t = 0.8927 - 0.00062t$ . The density and temperature coefficient were determined by careful measurements of the densities at two temperatures in a glass specific gravity bottle in comparison with pure mercury at the same temperatures. The constants for mercury were assumed, and the expansion of the glass was thus eliminated. The density at room temperature given by the formula was confirmed to 0.0001 by an independent determination made by Dr. von Siemens by means of a carefully calibrated Mohr's balance. The correct measurement of the pressures was an important part of the research, so that particular care was taken to obtain very accurate data for the density of the oil used. The levels of oil in the manometer were read to 0.01 cm. by a lens, care being taken to avoid parallax error. The oil was viscous, so that time had to be given for the levels to become constant, and as far as possible large changes of level were avoided. The tube immediately above the levels was, however, always wetted with oil before a reading was taken by a slight displacement of the levels of oil in the manometer. The manometer was screened from heat radiation coming from the gas burner, and the temperature of the oil determined by means of two calibrated thermometers lashed to the manometer, one at the top and the other at the bottom. The readings of these always agreed to  $0.1^{\circ}\text{C.}$

The atmospheric pressure, which coincides with the pressure  $p_2$  after

expansion, was determined to 0.01 cm. of mercury on the Fortin barometer in the main laboratory, all the usual corrections being applied, as well as a correction for the difference in altitude between the exposed mercury surface in the barometer and the oil surface in the manometer in the lower laboratory. The initial pressure  $p_1$  was found by adding to this corrected reading the mercury equivalent of the oil column. Both  $p_1$  and  $p_2$  were thus expressed in millimetres of mercury at standard level at 0° C. This is necessary, since the ratio of the pressures and not their difference is involved in the calculations.

The most important part of the apparatus was the arrangement used for the determination of the temperatures of the gas before and after expansion. To minimise the lag, a Wollaston wire of 0.001 to 0.002 mm. diameter was used, and the effects of the leads entirely eliminated by having a second shorter piece of the same wire attached to compensating leads, as in the method of Prof. Callendar. The length of this second wire necessary to ensure complete compensation was determined by trial, beginning with a short length, and increasing this until, after expansion, the galvanometer deflection no longer showed the "creeping" effect described on p. 31. With full compensation the galvanometer deflection occurred instantaneously, and remained perfectly steady for some seconds, then changing in the direction opposite to the expansion deflection. It was found that a length of wire equal to one-quarter to one-third the length of the main wire was required to effect complete compensation, *i.e.*, a much longer relative length than is necessary in ordinary thermometry with thicker wires. The platinum wires were supported by an arrangement to be described later, in the centre of the globe, with the longer loop hanging freely downwards, and the shorter loop in such a position that its projection in the plane of the leads did not cut the projections of any of the leads. In this way convection from the leads did not affect either loop of wire.

A long series of experiments, made with the object of finding the temperature coefficient of the thin wire, and thence of using the latter directly as a resistance thermometer, led to no satisfactory results, and the determination of temperature was finally effected in the manner described by Lummer and Pringsheim, *viz.*, by means of an auxiliary mercury thermometer in the water-bath. This has the great advantage that calibration of the resistance apparatus is rendered quite unnecessary, and that the results do not depend on any temperature function assumed for the platinum wires. The latter is of importance with such fine wires as were used, since the preliminary experiments indicated that their behaviour was not in accordance with the formula of Prof. Callendar, which is known to hold with great accuracy with thicker wires. The auxiliary mercury thermometer was graduated in

tenths of a degree, and was carefully calibrated in a vertical position with the normal thermometer No. 30,013 (1906) of the Reichsanstalt. Corrections for emergent stem, amounting to  $0.01^{\circ}$  to  $0.02^{\circ}$ , were applied, the readings being made to  $0.01^{\circ}$  by means of a lens. The thermometer was immersed in the water of the bath, being supported by a cork passing through a hole in the lid, and the readings were made by a lens on the part of the stem outside the lid. The emergent stem correction was applied only to that part of the stem outside the lid.

The arrangement for supporting the platinum wires is shown in fig. 2. Four copper wires, each enclosed in a glass capillary tube, *g*, passed through a wider glass tube, *D*, the ends being fused to short stout pieces of platinum wire, which were sealed through the glass at *C*, and projected outside about half an inch. To these the Wollaston wires (of excellent quality, as supplied by Hartmann and Braun, of Frankfurt a/M) were attached by solder. The silvered wire was first thoroughly softened by passing it backwards and forwards several times through a spirit-lamp flame. Two pieces were then cut off and bent into the two loops for the main piece and the piece for compensation. The compensation loop, *B*, was fairly narrow; the other, *A*, was broad and flat. The bent loops were then passed through the flame. When the wires were attached, the glass tube was fitted into a cork which fitted the outlet from the globe, and the leads to the bridge were attached. The silver was then removed from the platinum wire by electrolysis in a solution of potassium argentocyanide containing a considerable excess of potassium cyanide, using a cathode of silver plate. One accumulator was used, the glass tube being supported vertically in a clamp, with the loop of wire dipping into the solution in a beaker to the depth to which it was desired to remove the silver.

In this way the wire was freed from silver in from 10 to 15 minutes, and, since no gas was evolved, there was no danger of the fine wires being broken by gas bubbles buoying them up in the liquid, as is often the case in the slower and less certain method in which dilute nitric acid is used to remove the silver. The electrolysis was continued until the resistance of the loop remained constant. The position of the fine platinum wire was then shown by a fine black line joining the remaining parts of the silver leads. When the whole was carefully lifted from the solution, a black powder, possibly silver oxide, fell away readily from the platinum wire, which could then no longer be seen by the eye. The loop was then lowered carefully into hot distilled water in a beaker, allowed to stand for a few minutes, and again carefully removed. If the electrical resistance showed that the wire was still unbroken, the loop was immersed in hot dilute nitric acid

(one volume of acid to three of water), and the washing with water repeated two or three times. The two loops were treated separately, the large one first, as this was found to involve less danger of breakage. The washings must be carefully carried out, otherwise a film is likely to form on the wire in use, which alters its emissivity to such an extent as to vitiate the results. When examined by a good lens in a powerful light the loop showed a high polish, as it should do if the radiation correction is to be applied. The loops were then allowed to dry inside a large beaker with a loose cardboard cover. After standing for a few hours, with a little calcium chloride at the bottom of the beaker, the whole bolometer apparatus was fixed in position with the loops inside the globe, all draughts, shaking, and jarring being avoided. The glass lugs, E, shown in fig. 2, served to guide the tube through the neck of the globe. The cork was made gas-tight with marine glue, and the apparatus was ready. It is hardly necessary to say that many loops were broken, both in fitting and subsequently, but the method of preparation described is so much easier and more rapid than the ordinary method with nitric acid that these accidents were not very serious. Once the loops were in position in the globe, they were not likely to be ruptured even when fairly high excess pressures were released suddenly.

The four leads were carried to the resistance apparatus, H, fig. 1, consisting of a box of manganin coils by Hartmann and Braun, of Berlin, provided with rubbing-contacts on brass studs. To permit the inclusion of the compensating leads and an external resistance to increase the sensitiveness of the bridge, the thick wire leading from the set of high-resistance coils in the box to the end of the ratio-arms was divided and a pair of thick leads brought outside the box. These were connected with the compensating leads in series with a resistance box. The main leads from the longer platinum wire were connected to the ordinary terminals of the bridge. The bridge current was provided by an accumulator short-circuited through a Ruhstrat 515-ohm resistance from which a feeble current was taken by the sliding contact in series with a resistance of 1,000 ohms. It was ascertained that the measured resistance of the bolometer was not affected by variations within reasonable limits of the bridge current, so that there was no appreciable heating of the fine wire. The main wire in the bolometer was about 5 cm. long and had a resistance of about 1,000 ohms. In making the measurements the galvanometer circuit was kept closed so as to avoid disturbances due to thermoelectromotive forces.

The galvanometer was an Einthoven "Saitengalvanometer No. 1530" made by Edelmann of Munich, with a gold string, 0.005 mm. diameter, with a resistance of 106 ohms. The sensibility was  $10^{-8}$  ampère per scale division, and one-tenth of a scale division could be estimated with the objective and

eyepiece used. With the tension of the string employed the period was about 0.01 seconds, and the motion was perfectly dead-beat. The field magnets were actuated by a constant current of 2 ampères from a large accumulator battery. Connection with the bridge was made by a tapping-key for convenience in preliminary adjustment, but during the measurements this key was short-circuited by a mercury contact. All the keys were insulated on blocks of paraffin wax and the leads slung from glass tubes to avoid disturbances from stray currents. The galvanometer was supported on a stone slab and was earthed from the magnet system.

The initial temperature of the bath was raised to about 20° C. and maintained at this temperature for ten to fifteen minutes by heating occasionally for a few seconds. When the resistance and the reading of the manometer had both become perfectly steady, showing that the temperature of the gas in the globe had become uniform, the temperature of the bath was read on the mercury thermometer, and the manometer reading noted. The manometer tap, J, was then closed and the resistance on the bridge altered to such a value as was judged would correspond with that of the bolometer after the expansion had occurred. The battery current was put on, and (about fifteen seconds after closing J) the valve was released. The galvanometer, which, of course, had been deflected by the alteration of the bridge, then moved instantaneously to a position near the zero of the scale. This position was noted and the whole operation repeated with an initial pressure slightly higher or lower as was indicated by the deflection to one side or other of the zero in the previous expansion. The constancy of the zero, it may be mentioned, was confirmed repeatedly. When the deflection returned precisely to the zero after expansion the temperature of the bath and the manometer were carefully read, the water emptied from the bath by an injector pump, and cold water rapidly filled in. The stirrers were started and the temperature adjusted either by heating or by adding a little ice until the galvanometer with the bridge unaltered was again steadily at the zero. During this operation the barometer reading was taken. The temperature of the bath was then carefully read on the mercury thermometer and the measurement was complete. Two measurements could be made in one day when all was in order.

The criticism of Lummer and Pringsheim's method by Maneuvrier, that the use of the auxiliary thermometer was attended by the possibility of error in that the temperature of the gas in the globe was not equal to that of the water-bath, although *a priori* not very probable, was completely negatived by these experiments. The resistance could be exactly reproduced after 10 to 15 minutes when the temperature of the water-bath was altered to any



previously used value. A difference of  $0.01^{\circ}$  C. could readily have been detected. In addition, when the resistance became steady, the manometer also came to rest, and the corrected manometric reading always corresponded, within the limits of experimental error, with the resistance of the bolometer.

An actual experiment is described in full, omitting the preliminary adjustments of pressure:—

May 27, 1913. Air in Globe.

Initial resistance.	Final resistance.	Initial temperature (uncorrected).	Manometer mm. at $17.5^{\circ}$ .	Deflection from 0 after expansion.
ohms. 420.75 420.75	ohms. 410.05 410.05	$^{\circ}$ 20.00 20.00	121.09—5.64 120.90—5.80	+ 0.1 0

Barometer (corrected) = 759.7 mm. =  $p_2$ .

Final temperature of bath to correspond with 410.05 ohms =  $12.35^{\circ}$  (uncorrected).

Excess pressure =  $120.90 - 5.80 = 115.10$  cm. of oil at  $17.5^{\circ}$ .

Density of oil at  $17.5^{\circ} = 0.8927 - 17.5 \times 0.00062 = 0.8818$ .

Equivalent column of mercury at  $0^{\circ}$ (reduced) =  $115.10 \times 0.8818 / 1.3596$  mm. = 74.65 mm. Thus:—

Initial pressure =  $p_1 = 759.7 + 74.65 = 834.35$  mm.

Initial temperature =  $20.00 + \text{scale error} + \text{emergent stem correction}$   
 $= 20.00 + 0.02 + 0.01 = 20.03^{\circ}$ .

Final temperature =  $12.35 - 0.05 + 0.01 = 12.31^{\circ}$ .

$p_1 = 834.35$  mm.;  $p_2 = 759.7$  mm.;

$T_1 = 20.03 + 273.09 = 293.12$ ;  $T_2 = 12.31 + 273.09 = 285.40$ .

Thus,  $\gamma'$  (uncorrected for radiation and deviations from gas laws)

$$= \frac{\log p_1 - \log p_2}{\log p_1 - \log p_2 - (\log T_1 - \log T_2)} = 1.3981.$$

The experiments with carbon dioxide were made in the same way as those with air, except that the soda-lime tube was omitted in the purifying train. The gas was obtained from a cylinder of liquid. It was ascertained by special experiments that the gas was insoluble in the manometer oil, so that the density of the latter was obtained from the same formula as before. An analysis of the gas taken from the globe after all the experiments showed that it contained 1.5 per cent. by volume of air. The value of  $\gamma'$  for carbon dioxide (uncorrected for radiation) was therefore corrected by the subtraction

of 0.0015, which is just within the accuracy attainable by the method, viz., 1 part in 1000. The presence of air in commercial carbon dioxide has been referred to by other experimenters. On account of the large volumes of gas required, however, it was scarcely possible to use any other source of the gas.

The results of the experiments with air and carbon dioxide are recorded in Tables I to III below. The values of  $\gamma'$  are those calculated in the manner illustrated by the example. They require two corrections: (1) for radiation, (2) for the deviation of the gases used from the ideal state, to which alone equation (1) applies.

The radiation correction was determined by the method of Lummer and Pringsheim. The bolometer was carefully taken out of the globe, and both loops blackened by depositing platinum on them electrolytically from a solution of chloroplatinic acid containing a trace of lead acetate. They were washed, dried, and replaced in the globe. The amount of platinum deposited would not affect appreciably the thickness of the wires. With the thermometer used in the first series of experiments with air, the following result was obtained when blackened:—

$$p_1 = 828.41; \quad p_2 = 754.2; \quad T_1 = 293.12; \quad T_2 = 285.79; \\ \gamma' \text{ (uncorrected)} = 1.3703.$$

Hence the radiation correction was  $(1.4001 - 1.3703)/14 = 0.0021$ . This is the value found by Lummer and Pringsheim and by Makower. This was to be expected, since the rise in temperature produced by radiation depends, in the same gas, only on the nature of the bolometer surfaces and not on the dimensions of the other part of the apparatus. The value for carbon dioxide is, strictly speaking, 0.0021 multiplied by the square of the ratio of the refractive indices of carbon dioxide and air; this correction, however, is so small that the value 0.0021 may be used for the different gases.

Air. First Series, May, 1913. Diameter of thermometer wire = 0.001 mm.

$p_1$ mm.	$p_2$ mm.	$T_1$ .	$T_2$ .	$\gamma'$ (uncorrected).
800.90	755.6	292.59	287.75	1.4015
795.27	750.1	292.59	287.75	1.3992
835.68	761.2	293.12	285.38	1.4019
834.35	759.7	293.12	285.40	1.3981
831.10	756.5	293.12	285.38	1.3978
831.78	757.4	293.12	285.38	1.3999
829.55	755.8	293.12	285.38	1.3993
828.20	754.2	293.12	285.38	1.4004
Mean $\gamma' =$				1.4000

Air. Second Series. June, 1913. Diameter of thermometer wire = 0.002 mm.

$p_1$ mm.	$p_2$ mm.	$T_1$ .	$T_2$ .	$\gamma'$ (uncorrected).
819.93	750.8	293.12	285.83	1.4004
819.87	750.8	293.12	285.83	1.4009
818.67	751.2	293.12	286.03	1.3980
807.20	753.4	293.12	287.39	1.4011
804.90	753.8	293.12	287.67	1.4008
Mean $\gamma' =$				1.4002

Carbon Dioxide. July, 1913. Diameter of thermometer wire = 0.002 mm.

$p_1$ mm.	$p_2$ mm.	$T_1$ .	$T_2$ .	$\gamma'$ (uncorrected).
828.65	757.1	293.12	287.15	1.2952
828.72	757.1	293.12	287.15	1.2948
827.17	755.7	293.12	287.18	1.2980
830.54	756.6	293.12	286.92	1.2975
829.27	756.1	293.12	286.97	1.2979
830.44	756.6	293.12	286.92	1.2980
830.40	756.6	293.12	286.92	1.2982
834.33	756.4	293.12	286.65	1.2947
834.20	756.4	293.12	286.65	1.2954
834.31	756.4	293.12	286.65	1.2948
835.33	756.3	293.12	286.51	1.2979
835.32	756.3	293.12	286.51	1.2979
Mean $\gamma' =$				1.2964

Both values require correction for radiation; that for carbon dioxide requires correction for the 1.5 per cent. of air present in the gas. The values of  $\gamma'$ , corrected for radiation, but not for deviations from the gas laws, are:—

$$\text{Air at } 17^\circ \text{ C. } \gamma' = 1.4001 + 0.0021 = 1.4022 \pm 0.0003.$$

$$\text{Carbon dioxide at } 17^\circ \text{ C. } \gamma' = 1.2964 - 0.0015 + 0.0021 = 1.2970 \pm 0.0003.$$

Equations (1) and (2) were deduced on the assumption of the laws of ideal gases, which are not fulfilled by air and carbon dioxide. The values of  $\gamma'$  given above therefore require correction for the deviation of the respective gases from the ideal state. Lummer and Pringsheim, in place of the absolute temperature  $T = 273.09 + t^\circ \text{ C.}$ , used a temperature defined by  $T = t^\circ \text{ C.} + 1/\alpha$ , where  $\alpha$  is the coefficient of expansion of the gas. This method, whilst giving almost the correct result with air, gives, when applied to carbon dioxide, a different correction from that applied in the present research.

The value of  $\gamma = c_p/c_v$  may be calculated from  $\gamma'$ , calculated from the experimental results by equation (2), by making use of the characteristic equation of D. Berthelot :—\*

$$\left(p + \frac{a}{Tv^2}\right)(v-b) = RT, \quad (3)$$

which reproduces with great accuracy the behaviour of gases under moderate pressures. The constants  $a$  and  $b$  are calculated from the critical constants of the gas as follows :—

$$a = \frac{27}{64} R^2 \frac{T_c^3}{p_c}; \quad b = v_c/4. \quad (4)$$

The correction of  $\gamma'$  is then given by the equation

$$\gamma = \gamma' \left[ 1 + (\gamma' - 1) \frac{27}{32} \pi \tau^3 \right] = \gamma' \phi, \quad (5)$$

where  $\pi = (p_1 + p_2)/2p_c$  and  $\tau = 2T_c/(T_1 + T_2)$ . (6)

In the case of air,  $p_c = 39.3$  atm.,  $T_c = 132.6^\circ$ . In the case of carbon dioxide,  $p_c = 72.85$  atm.,  $T_c = 304^\circ$ . The values of  $\phi$  at 1 atm. pressure and  $17^\circ$  C. are therefore, for air, 1.00083, and for carbon dioxide, 1.0040. From these values, and the values of  $\gamma'$  given above, we find :—

$\gamma = c_p/c_v$  for air at  $17^\circ$  and 1 atm. pressure =  $1.4034 \pm 0.0003$ ,

$\gamma = c_p/c_v$  for carbon dioxide at  $17^\circ$  C. and 1 atm. pressure =  $1.3022 \pm 0.0003$ .

In comparing the above values of  $\gamma$  with those of former investigators, account must be taken of the fact that the latter have been obtained at different temperatures, and that in some cases they require corrections. These corrections arise in consequence of (i) incorrect values adopted for the value of  $\gamma$  for air when comparisons of the wave-length of sound in air and in the gas have been made; (ii) incorrect values of the densities of the gases assumed in the calculations of  $\gamma$  from the velocity of sound; (iii) the assumption that the gases, even carbon dioxide, were ideal;† (iv) the assumption that  $C_p - C_v$  is equal to  $R$ , the gas constant, for actual gases, when the molecular heats  $C_p$  and  $C_v$  are calculated from the ratio  $\gamma$ . The following values of  $\gamma$  for air have been corrected when necessary :—

\* 'Mémoires Bureau Internat. Poids Mesures,' vol. 13 (1907); Nernst, 'Theoretische Chemie,' 7th Auflage, p. 241 (1913).

† This erroneous assumption was made by Moody in the case of carbon dioxide.

Observer.	Temperature.	$\gamma'$ .	$\phi$ .	$\gamma$ .
Roentgen.....	Not stated	—	1·0000*	1·4053 $\pm$ 0·0005
Lummer and Pringsheim ...	10° C.	1·4013	1·00083	1·4025 $\pm$ 0·0004
Makower .....	Not stated	1·401	1·00083	1·402
Moody .....	25° C.	1·4011	1·00083	1·4021 $\pm$ 0·0005
Partington .....	17° C.	1·4023	1·00083	1·4034 $\pm$ 0·0003

\* The results of Roentgen, calculated by equation (1), require no correction.

The results for carbon dioxide are given below :—

Observer.	Temperature.	$\gamma'$ .	$\phi$ .	$\gamma$ .
Roentgen.....	19·5° C.	—	1·0000	1·3051
Lummer and Pringsheim ...	10° C.	1·2958	1·0043	1·3014
Moody .....	25° C.	1·3003	1·0037	1·3051
Partington .....	17° C.	1·2970	1·0040	1·3022 $\pm$ 0·0003

The specific heats at constant volume and at constant pressure may be calculated from the ratio  $c_p/c_v = \gamma$  when the difference  $c_p - c_v$ , or, more conveniently,  $M(c_p - c_v) = C_p - C_v$ , where  $M$  is the molecular weight, is known. This may be obtained from Berthelot's equation :—

$$C_p - C_v = 1\cdot985 \left( 1 + \frac{27}{16} \pi \tau^3 \right) = 1\cdot985 \phi' \text{ gram. cal.}, \quad (7)$$

where  $\pi$  and  $\tau$  have the values given by (6).

In the case of air at 17°,  $\phi' = 1\cdot0042$ , hence  $C_p - C_v = 1\cdot989$  grm. cal. The values for 1 grm. of air are:  $c_p - c_v = 1\cdot989/28\cdot99 = 0\cdot0686$  grm. cal.,  $c_v = 0\cdot0686/0\cdot4034 = 0\cdot1701$  grm. cal.,  $c_p = 0\cdot1701 + 0\cdot0686 = 0\cdot2387$  grm. cal.

The value of  $c_p$  for air calculated from the results of Lummer and Pringsheim is 0·2397 grm. cal. The above values may now be compared with the values of  $c_p$  determined calorimetrically.

Regnault\* found the mean specific heat of air to be practically constant from  $-30^\circ$  to  $200^\circ$  C., measured on the air thermometer, the mean result being 0·2375 grm. cal. Leduc† pointed out that this result requires to be increased by 1/160 of its value on account of the neglect of Regnault to take account of the effect (which is stated by Regnault) of the expansion of the air in passing from the heater to the calorimeter. The corrected value of Regnault is then 0·2390, in agreement with the value determined by Wiedemann,‡ 0·2389, and with the value calculated from the value of  $\gamma$  found

\* 'Mémoires de l'Académie,' vol. 26 (1862).

† 'Comptes Rendus,' vol. 126, p. 1860 (1898).

‡ 'Annalen der Physik,' vol. 157, p. 1 (1876).

in the present research. More recent experimenters have obtained values for  $c_p$  greater than that of Regnault, and each experimenter has applied new corrections to Regnault's value, to bring it into almost perfect accord with his own result.

W. F. G. Swann\* used the method of "constant-flow" calorimetry invented by Prof. Callendar, and applied by him and Dr. Barnes in an accurate determination of the specific heat of water. The values of  $c_p$  for air found by Swann were 0.2417 at 20° (extreme values 0.2408 to 0.2419) and 0.2430 at 100° (extreme values 0.2418 to 0.2427). Using the same method as Swann, Scheel and Heuse† obtained the value 0.2403 at 20°, which is about 0.6 per cent. smaller than that obtained by Swann. More recently, Holborn and Jacob,‡ by the same method, obtained 0.2415 at 59°, which is 0.4 per cent. lower than Swann's value, 0.2423, interpolated for that temperature. The values of  $c_p$  found by different experimenters *using the same method* are therefore in fairly satisfactory agreement. The value of  $c_p/c_v$  for air, calculated from Swann's value of  $c_p$  at 20°, however, is 1.397, which is lower than that found in any recent accurate determination of  $\gamma$  by the method of adiabatic expansion or by the velocity of sound.

In the calculation of  $\gamma$  from the velocity of sound it is also necessary to take account of deviations from the gas laws. Berthelot's equation then leads to the formula:—

$$\gamma = \frac{u^2 M}{RT} \left[ 1 - \frac{9}{64} \pi \tau (1 - 6\tau^2) \right] = \gamma' \phi'', \quad (8)$$

where  $M$  = molecular weight ( $O_2 = 32$ ),  $R$  is the gas constant,

$$8.315 \times 10^7 \text{ erg/}^\circ \text{C.},$$

$\pi$  and  $\tau$  have the values defined by equations (6), and  $u$  is the velocity of sound in centimetres per second. The value  $\gamma'$  calculated on the (incorrect) assumption of the laws of ideal gases is, therefore, corrected by multiplication by  $\phi'' = 1 - 9/64 \pi \tau (1 - 6\tau^2)$ . In the case of air at 0° C.,  $\phi'' = 1.00072$  and  $\gamma = 1.27805 \times 10^{-9} u^2$ . With the value of  $\gamma$  found in the present research, the velocity of sound in dry air at 0° is calculated as 331.38 metres per second.

The velocity of sound in free air at 0° was found by the Bureau des Longitudes as 331.2 m./sec., which gives  $\gamma = 1.402$ . The results of Hebb§ appear to be the most accurate in this field; in two determinations he found  $u_0 = 331.44$ , giving  $\gamma = 1.4039$  (1.4031), and  $u_0 = 331.28$ , giving

\* 'Phil. Trans.,' A, vol. 210, p. 199 (1911).

† 'Annalen der Physik,' vol. 37 p. 79 (1912); vol. 40, p. 473 (1913).

‡ 'Sitzungsber. Berlin Akad.,' p. 213 (1914).

§ 'Phys. Review,' vol. 20, p. 89 (1905); 'Trans. Roy. Soc. Canada,' vol. 13, sec. 3, p. 101 (1919).

$\gamma = 1.4026$  (1.4026), respectively. The results have been corrected according to Berthelot's equation; the figures given by Hebb, calculated by Van der Waals's equation, are given in brackets.

The velocity of sound in long conduits, as determined by Regnault and by Violle and Vautier, and corrected by Stevens,\* is 331.3, giving  $\gamma = 1.403$ . Szathmari† gives 331.57, from which  $\gamma = 1.4050$ . These results are without doubt less accurate than those of Hebb. The velocity of sound in small tubes is also probably less accurate than that determined in free air. Webster Low‡ as corrected by Stevens found  $u_0 = 331.4$  m./sec., to which  $\gamma = 1.4036$  corresponds; Blaikley,§ in the case of the widest tubes, found  $u_0 = 331.4$ , or  $\gamma = 1.4036$ ; Stevens obtained  $u_0 = 331.32$ , or  $\gamma = 1.4029$ ; Thiesen|| gives  $u_0 = 331.92$ , or  $\gamma = 1.4080$ ; whilst the result of Wüllner, corrected by Leduc, is  $u_0 = 331.8$  or  $\gamma = 1.403$  (from the formula of Leduc¶). Apart from the unusually high value obtained by Thiesen, all these results are in excellent agreement with the value of  $\gamma$  determined in the present research. Particular reliance is placed on the results of Hebb, which appeared after the research had been completed. A value of  $\gamma$  for air somewhat in excess of 1.400, and very probably 1.403, seems to be, from the results obtained by the method of adiabatic expansion and by the velocity of sound, very near the true value. The figure 1.397, obtained by calculation from the value of  $c_p$  obtained by the method of constant flow calorimetry applied to gases, finds no support in any other method, and one cannot escape the suspicion that some source of constant error in this method, when applied to gases, has been overlooked.

The specific heats of carbon dioxide may be calculated from the value  $\gamma = 1.3022$  at  $17^\circ$  by means of equation (8). In this case the value of  $C_p - C_v$  is found to be  $1.985 \times 1.0266 = 2.038$ . Thus,  $C_v = 2.038/0.3022 = 6.744$ , and  $C_p = 6.744 + 2.038 = 8.782$ . The corresponding values per gramme are:— $c_v = 0.1531$  and  $c_p = 0.1996$  grm. cal. The following values of  $c_p$  for carbon dioxide, in some cases interpolated, have been obtained by calorimetric methods. Regnault,  $0.1870$  ( $0^\circ$ ),  $0.1927$  ( $20^\circ$ ),  $0.2145$  ( $100^\circ$ ); Wiedemann,  $0.1952$  ( $0^\circ$ ),  $0.1989$  ( $20^\circ$ ),  $0.2168$  ( $100^\circ$ ); Swann,  $0.2020$  ( $20^\circ$ ),  $0.2214$  ( $100^\circ$ ); Scheel and Heuse,  $0.2018$  ( $20^\circ$ ); Holborn and Henning,\*\*  $0.2010$  ( $0^\circ$ ),  $0.2013$  ( $20^\circ$ ),  $0.2163$  ( $100^\circ$ ). There are appreciable differences between these

\* 'Verhandl. Deutsch. Physik. Ges.', vol. 3, p. 54 (1901).

† 'Annalen der Physik,' vol. 2, p. 418 (1877).

‡ 'Annalen der Physik,' vol. 52, p. 641 (1894); Stevens, 'Verhandl. Deutsch. Physik. Ges.', vol. 3, p. 54 (1901).

§ 'Phys. Soc. Proc.', vol. 6, p. 228 (1884-5).

|| 'Annalen der Physik,' vol. 25, p. 506 (1908).

¶ 'Comptes Rendus,' vol. 127, p. 1201 (1898).

\*\* 'Annalen der Physik,' vol. 23, p. 809 (1907).

values. The temperature coefficient of  $c_p$  for carbon dioxide has also been variously estimated: Regnault, 0.0275; Wiedemann, 0.0217; Holborn and Henning, 0.0133; Swann, 0.0240, all per 100° C. If Wiedemann's value is adopted, the mean result for  $c_p$  at 17° C. from the values of Wiedemann and of Scheel and Heuse becomes 0.1997, which is in agreement with the value calculated from  $\gamma$  found in the present research. The values of  $c_p$  for carbon dioxide found by the method of constant-flow calorimetry are also appreciably greater than those found by any other method.

A comparison of the values of  $\gamma$  determined at different temperatures is difficult on account of the uncertainty in the value of the temperature coefficient of  $\gamma$ . Wüllner's results for the velocity of sound in carbon dioxide at 0° and 100° indicate that this coefficient is 0.035 per 100°. The corresponding value calculated from the measurements of Holborn and Henning of  $c_p$ , and the values of  $C_p - C_v$  from equation (7), is 0.0337. Swann's figures give the higher value 0.0485.

The velocity of sound in carbon dioxide at 17° may be calculated from the value  $\gamma = 1.3022$  by means of equation (8). The latter gives  $\gamma = 1.8453 \times 10^{-9} u^2$  at 17°, hence  $u_{17}$  for carbon dioxide is 265.65 m./sec. Calculations of the specific heats of, and velocities of sound in, carbon dioxide at temperatures other than 17° are omitted on account of the uncertainty of the temperature coefficient of  $c_p$ .

A portion of the absorption of heat represented by  $c_p$  in the case of an imperfect gas is used in performing intermolecular work due to attractions existing between the gas molecules. The correction of the specific heats to the ideal state is of interest when comparisons of the energies of gas molecules are instituted, since in this case the work due to intermolecular attraction is extraneous. The correction can be made by the following formula, derived from Berthelot's equation:—

$$C_v^\circ (\text{ideal}) = C_v - \frac{27}{32} R\pi\tau^3, \quad (9)$$

$$C_p^\circ (\text{ideal}) = C_v^\circ + 1.985 \text{ gm. cal.}, \quad (10)$$

$$\gamma_0 (\text{ideal}) = C_p^\circ / C_v^\circ, \quad (11)$$

The values of  $(27/64) \times R\pi\tau^3$  at 17° are: for air, 0.0021; for carbon dioxide 0.0132. Thence:—

	$c_v$ .	$c_p$ .	$C_v$ .	$C_p$ .	$C_v^\circ$ .	$C_p^\circ$ .	$\gamma$ .	$\gamma_0$ .
Air at 17° C. ....	0.1701	0.2387	4.981	6.920	4.929	6.914	1.4084	1.4027
Carbon dioxide at 17° C.	0.1581	0.1996	6.744	8.782	6.731	8.716	1.3022	1.2949



*On the Currents induced in a Conductor by the Passage of a  
Mass of Magnetic Material over it.*

By E. S. BIELER, M.Sc., 1851 Scholar of McGill University.

(Communicated by Sir E. Rutherford, F.R.S.—Received April 22, 1921.)

[PLATE 1.]

The investigation of the currents induced in a conductor by the passage of a mass of magnetic material over it is a matter of some considerable interest. In the simple case where the mass is in the form of a spherical shell, the problem can be investigated mathematically, and the motion of the spot of a galvanometer connected to such a conductor can be deduced. It has occurred to the writer to compare the results of a mathematical investigation with those of experiments carried out in the laboratory on a small scale. It is the object of the present paper to give a summary of both the theory and the experimental confirmation.

THEORETICAL INVESTIGATION.

*A. The Induced Electromotive Force.*

Consider an iron shell (fig. 1) of internal and external diameters  $a$  and  $b$ , and of permeability  $\mu$ , passing with velocity  $v$  over an infinitely long straight conductor at depth  $d$  below the level of its centre. Take axes through the centre, the Y-axis being vertical and the X- and Z-axes being horizontal, the one perpendicular, the other parallel to the direction of the conductor. Let  $l, m, n$  be the direction cosines of  $F$ , the earth's field, and let  $\alpha$  be the angle between the Z-axis and the direction of motion of the shell.

By the application of spherical harmonics it is easily proved that the magnetic potential at a point  $(x, y, z)$  at a distance  $r$  from the origin is given by

$$V = F(lx + my + nz)(1 + \lambda/r^3),$$

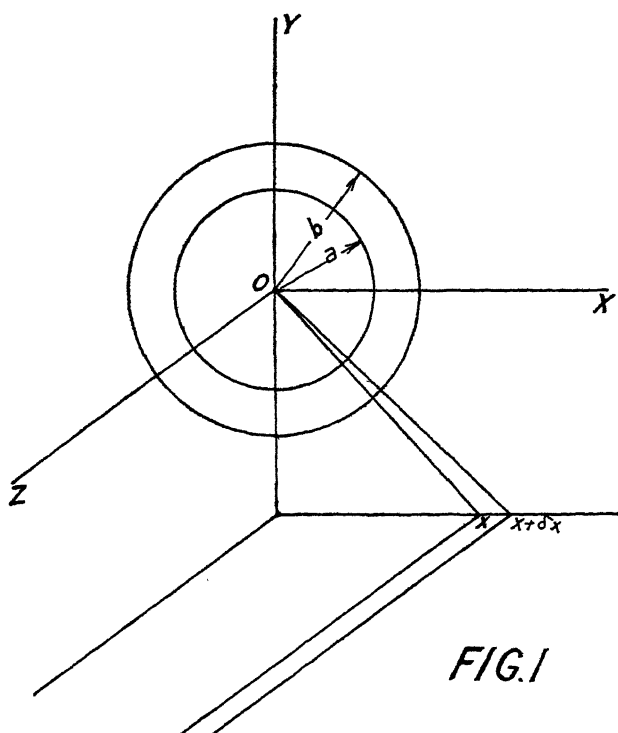
where

$$\lambda = -(b^3 - a^3) \frac{(2\mu + 1)(\mu - 1)}{9\mu + 2(\mu - 1)^2(1 - a^3/b^3)}.$$

The term  $F(lx + my + nz)$  is due to the earth's undisturbed field. The other term gives the potential of the disturbance.

Instead of considering the conductor as stationary and the shell as moving past it, it is simpler to reduce the shell to rest, and to consider the conductor as cutting the field due to the disturbance, that is, the field derived from the potential

$$V' = F \frac{\lambda(lx + my + nz)}{r^3}.$$



At time  $t$  let  $x$  be the horizontal distance of the shell from the conductor. In the interval  $\delta t$ ,  $x$  has increased to  $x + \delta x$ , and the number  $N$  of tubes of induction cut by the conductor in the interval is given by

$$\delta N = \left( \int_{-\infty}^{\infty} \frac{\partial V'}{\partial y} dz \right) dx.$$

The E.M.F. induced in the conductor is therefore given by

$$\begin{aligned} E &= -dN/dt \\ &= -dN/dx \cdot dx/dt \\ &= -\left( \int_{-\infty}^{\infty} \frac{\partial V'}{\partial y} dz \right) v \sin \alpha \\ &= -F\lambda v \sin \alpha \int_{-\infty}^{\infty} \frac{1}{r^3} \left( m - \frac{3y(lx + my + nz)}{r^2} \right) dz \\ &= -2F\lambda v \sin \alpha \frac{m(x^2 - d^2) - 2lxd}{(x^2 + d^2)^3}. \end{aligned} \tag{1}$$

B. *The Deflection produced in a critically damped Galvanometer.*

It will be assumed that the galvanometer is critically damped, a condition which can always be secured in a moving coil instrument by introducing a suitable shunt or series resistance.

Let  $A$  be the total area of the turns of a galvanometer coil suspended in a field of strength  $H$ . Let  $R$  be the total resistance in the galvanometer circuit,  $K$  the moment of inertia of the suspended system, and  $\tau$  the directing couple of the suspension for unit angular deflection.

If  $\theta$  represent the angular deflection of the moving system,  $i$  the current at any time, and  $E$  the impressed electromotive force, the two following equations are obtained at once from the mechanical and electrical conditions respectively,

$$K \frac{d^2\theta}{dt^2} - AH i + \tau \theta = 0, \quad (2)$$

$$E = Ri + AH \frac{d\theta}{dt}. \quad (3)$$

Eliminating  $i$  between (2) and (3), we obtain

$$\frac{d^2\theta}{dt^2} + \frac{A^2H^2}{RK} \frac{d\theta}{dt} + \frac{\tau}{K} \theta = \frac{AH}{RK} E. \quad (4)$$

The galvanometer will be critically damped, provided that  $R$  has been so adjusted that

$$(A^2H^2/RK)^2 = 4\tau/K,$$

that is, if

$$R = A^2H^2/2\sqrt{(\tau K)}.$$

If we now write  $n = A^2H^2/2RK = \sqrt{(\tau/K)}$ , equation (4) reduces to

$$\frac{d^2\theta}{dt^2} + 2n \frac{d\theta}{dt} + n^2\theta = (2n/AH) E,$$

or

$$(D+n)^2\theta = (2n/AH) E. \quad (5)$$

The values of the coefficients  $n$  and  $2n/AH$  are easily obtained by two simple observations on the galvanometer.

For a steady deflection, (5) reduces to  $n^2\theta = (2n/AH) E$ , that is,

$$\theta/E = 2/nAH. \quad (6)$$

Thus,  $2/nAH$  is the sensitivity in radians per unit E.M.F. for a steady deflection.

Also, if the galvanometer is allowed to swing on open circuit, the motion is given by

$$\frac{d^2\theta}{dt^2} + n^2\theta = 0,$$

and consequently the period  $T$  by

$$T = 2\pi/n. \quad (7)$$

Thus, by means of (6) and (7), we can evaluate the constants of (5) for the voltage sensitivity and the period of the galvanometer.

If we can solve (5) in the case where  $E$  is given by equation (1), we are

able to deduce the actual motion of the galvanometer spot due to the electromotive force induced in a conductor by the passage of a spherical shell of iron over it.

Substituting in (5) for the value of  $E$  given by (1), we obtain

$$(D+n)^2\theta = -(4n/AH) F\lambda v \sin \alpha (m(x^2-d^2)-2lnd)/(x^2+d^2)^2,$$

which, on replacing  $x$  by its value  $v \sin \alpha t = v't$ , reduces to

$$\begin{aligned} (D+n)^2\theta &= -(4n/AH) F\lambda v' (m(v'^2t^2-d^2)-2lv'td)/(v'^2t^2+d^2)^2 \\ &= -M (m(t^2-p^2)-2ltp)/(t^2+p^2)^2, \end{aligned} \quad (8)$$

where  $p = d/v'$  and  $M = 4nF\lambda/AHv'$ .

Now, it is easily found by the method of "Variation of Parameters,"\* that the solution of

$$(D+n)^2\theta = f(t)$$

$$\text{is} \quad \theta = \{t \int e^{nt} f(t) dt - \int t e^{nt} f(t) dt\} e^{-nt}. \quad (9)$$

Since  $f(t)$  is of the form

$$f(t) = -M (m(t^2-p^2)-2ltp)/(t^2+p^2)^2,$$

the solution will contain the four unknown integrals

$$\int \frac{t^3}{(t^2+p^2)^2} e^{nt} dt, \quad \int \frac{t^2}{(t^2+p^2)^2} e^{nt} dt, \quad \int \frac{t}{(t^2+p^2)^2} e^{nt} dt, \quad \int \frac{1}{(t^2+p^2)^2} e^{nt} dt.$$

It would be no simple task to evaluate these for various values of  $n$  and  $p$  over a considerable range of  $t$ , and we shall have to restrict ourselves to the special case where  $p = 1/n$ .

If we write  $nt = y$ , the four above integrals reduce to

$$\begin{aligned} I_1 &= \int_{-\infty}^y \frac{y^3}{(y^2+1)^2} e^y dy, \\ I_2 &= \int_{-\infty}^y \frac{y^2}{(y^2+1)^2} e^y dy, \\ I_3 &= \int_{-\infty}^y \frac{y}{(y^2+1)^2} e^y dy, \\ I_4 &= \int_{-\infty}^y \frac{1}{(y^2+1)^2} e^y dy, \end{aligned} \quad (10)$$

where the limits have been put in to satisfy the conditions  $\theta = 0, \dot{\theta} = 0$  at infinity.

The evaluation of these integrals will be made somewhat simpler if we define two other integrals,

$$\begin{aligned} I_5 &= \int_{-\infty}^y \frac{y}{y^2+1} e^y dy = I_1 + I_3, \\ I_6 &= \int_{-\infty}^y \frac{1}{y^2+1} e^y dy = I_2 + I_4, \end{aligned}$$

\* Forsyth, 'Differential Equations,' 4th ed., § 65.

The first three integrals may be written down in terms of the simpler integrals  $I_4$ ,  $I_5$ , and  $I_6$ ,

$$I_3 = \int_{-\infty}^y \frac{y}{(y^2+1)^2} e^y dy = -\frac{1}{2} \int_{-\infty}^y e^y d\left(\frac{1}{y^2+1}\right) = \frac{1}{2} I_6 - \frac{e^y}{2(y^2+1)},$$

$$I_2 = I_6 - I_4,$$

$$I_1 = I_5 - I_3 = I_5 - \frac{1}{2} I_6 + \frac{e^y}{2(y^2+1)}.$$

Substituting  $y$  for  $nt$  in (9) and (10) and writing  $p = 1/n$ , we obtain

$$\theta = \{(y/n^2) \int e^y \phi(y) dy - (1/n^2) \int y e^y \phi(y) dy\} e^{-y}, \quad (11)$$

where

$$\phi(y) = -n^2 M \frac{m(y^2-1)-2ly}{(y^2+1)^2}.$$

If we use this value of  $\phi(y)$  in (11), we finally get for  $\theta$  in terms of  $I_4$ ,  $I_5$ , and  $I_6$ ,

$$\begin{aligned} \theta &= M \{ m \{ [2yI_4 - (y+1)I_6 + I_5] e^{-y} + 1/(y^2+1) \} \\ &\quad + l \{ [(y-2)I_6 + 2I_4] e^{-y} - y/(y^2+1) \} \} \\ &= m\theta_1 + l\theta_2. \end{aligned} \quad (12)$$

The values of  $I_4$ ,  $I_5$ , and  $I_6$  at intervals of 0.6 from -4.8 to 7.2 are given in Table I and were calculated as follows:—The integrals between the limits  $-\infty$  and 0 were first worked out numerically from formulæ involving the sine- and cosine-integrals, given by Bierens de Haan.\* The integrand was then computed for values of the variable at intervals of 0.15 and the integrals evaluated at intervals of 0.6 by the use of Simpson's rule for five equidistant ordinates, viz.,

$$\int_{-2h}^{+2h} y dx = \frac{2}{45} h (7y_1 + 32y_2 + 12y_3 + 32y_4 + 7y_5),$$

where  $h$  is the interval between successive ordinates, and  $y_1$ ,  $y_2$ ,  $y_3$ ,  $y_4$  and  $y_5$  are the values of the integrand at each ordinate. The computations were carried out with the aid of an excellent Brunsviga calculating machine kindly lent by Mr. Richmond, of the Ballistic Office.

In addition to the integrals  $I_4$ ,  $I_5$  and  $I_6$ , Table I gives the values of  $\theta_1/M$

\* 'Verhand. der Kon. Akad. van Wet.,' Part IV, 1858, Table 130, formulæ 4 and 5; Table 131, formula 9; and 'Nouvelles Tables d'Intégrales Définies,' 1867, Table 91, formulæ 7 and 8; Table 92, formula 6.

(Formula 9, Table 131, of the 'Verhandeligen' is correct as it stands, namely,

$$\begin{aligned} \int_0^\infty \frac{e^{-px}}{(x^2+q^2)^2} dx &= 1/29^3 [\text{ci}(pq) \cdot \sin(pq) - \text{si}(pq) \cdot \cos(pq) + \frac{1}{2}\pi \cdot \cos(pq) \\ &\quad - pq \{ \text{ci}(pq) \cdot \cos(pq) + \text{si}(pq) \cdot \sin(pq) - \frac{1}{2}\pi \cdot \sin(pq) \}]. \end{aligned}$$

The minus sign before the  $pq$  has been changed by mistake to a plus sign in the "Nouvelles Tables," Table 92, formula 6.)

and  $\theta_2/M$ . These deflections are also plotted in the graphs of figs. 2 and 3. In each case the dotted curve represents the E.M.F., and the full curve the resulting galvanometer deflection. Fig. 2*a* corresponds to the case  $l = 0$ ,  $m = 1$ ; fig. 2*b* to  $l = 1$ ,  $m = 0$ ; and fig. 3 to  $l = \sin \delta/\sqrt{(2)}$ ,  $m = \cos \delta$ , where  $\delta$  is the dip, here equal to  $75^\circ$ .

Table I.

$y$ .	$I_1 = \int_{-\infty}^y \frac{1}{(y^2+1)^2} e^y dy.$	$I_5 = \int_{-\infty}^y \frac{y}{y^2+1} e^y dy.$	$I_6 = \int_{-\infty}^y \frac{1}{y^2+1} e^y dy.$	$\frac{\theta_1}{M}.$	$\frac{\theta_2}{M}.$
-4.8	0.000003	-0.00139	0.000236	0.0216	—
-4.2	0.000019	-0.00283	0.000560	0.0271	-0.0038
-3.6	0.000068	-0.00582	0.001336	0.0352	-0.0109
-3.0	0.000236	-0.01211	0.00327	0.0404	-0.0189
-2.4	0.000862	-0.02559	0.00885	0.0491	-0.0312
-1.8	0.00364	-0.05485	0.02264	0.0658	-0.0520
-1.2	0.01802	-0.11789	0.06632	0.0878	-0.0930
-0.6	0.10232	-0.23793	0.20888	0.0742	-0.1756
0.0	0.48241	-0.34338	0.62145	-0.0352	-0.2781
0.6	1.1344	-0.11439	1.35078	-0.2335	-0.2338
1.2	1.5890	0.70171	2.1644	-0.3356	-0.0563
1.8	1.8481	1.94917	2.9947	-0.2717	0.0875
2.4	2.0175	3.8653	3.9043	-0.1728	0.1527
3.0	2.1483	6.7977	4.9862	-0.0872	0.1527
3.6	2.2639	11.3541	6.3613	-0.0277	0.1440
4.2	2.3771	18.5216	8.2003	0.0087	0.1166
4.8	2.4970	30.0423	10.7579	0.0274	0.0893
5.4	2.6313	48.8208	14.4265	0.0350	0.0662
6.0	2.7917	79.6739	19.3206	0.0364	0.0483
6.6	2.9897	130.831	27.6295	0.0316	0.0329
7.2	3.2427	216.311	36.6947	0.0278	0.0226

### EXPERIMENTAL CONFIRMATION.

The truth of the above results was tested by experiments carried out on a small scale in the Electrical Measurements Laboratory at McGill University by the use of a 16-lb. spherical iron shot and a coil of many turns connected to a reflecting galvanometer, whose deflections were registered photographically.

The coil, on a square frame of 125 cm. side, had 200 turns of No. 28B. and S. copper wire, wound close together, to give a circular section of about 1 cm. diameter. Its resistance, 221.5 ohms, was made up to 224 ohms, the critical damping resistance of the galvanometer.

The galvanometer was a moving coil instrument of 8 seconds free period, whose sensitivity, when in series with its critical damping resistance, was 1.63 mm. per microvolt at 1 metre.

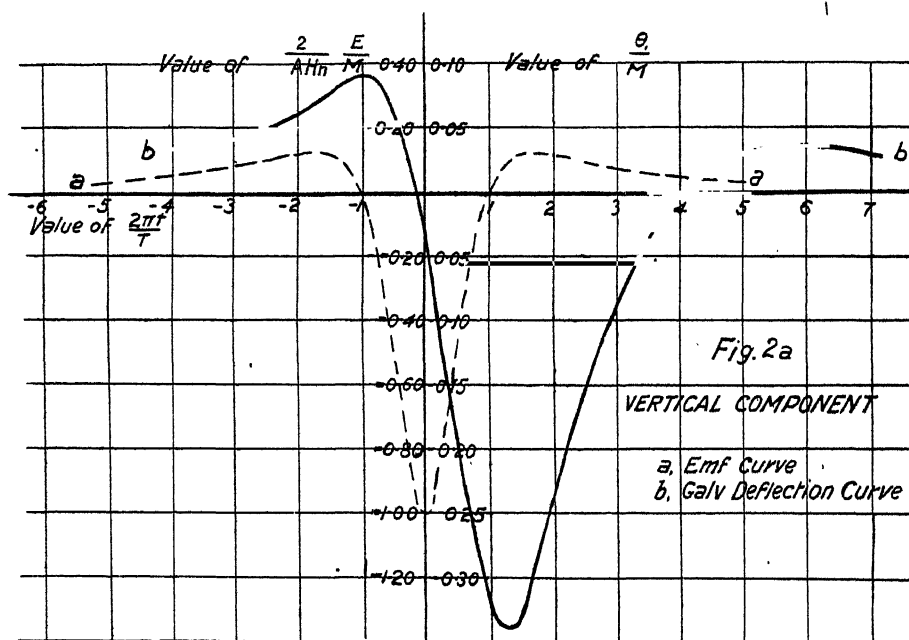
The iron sphere, an iron shot kindly lent by Spalding and Co., proved to have excellent magnetic qualities. It exhibited practically no permanent

magnetism after lying in the same position in the earth's field for several days.

The galvanometer deflection was recorded by means of a camera consisting of a box with a long horizontal slit. Metal cylinders, actuated by clockwork, unwound a roll of sensitised paper past the slit. A time-mark was made every second by a small pea-lamp connected to a clock. In addition, the pea-lamp circuit was made for an instant as the shot came past three contacts, one directly opposite the side of the coil, and the other two 40 cm. before and after, respectively.

Experiments were carried out for three different positions of the coil.

A. *Vertical Component*.—The shot was made to travel horizontally in a magnetic east and west direction over one side of the coil, pointing magnetic north and south. The horizontal component of the earth's field acted along the side of the coil, and the vertical component alone was effective. In this case,  $l = 0$  and  $m = \sin \delta = \sin 75^\circ$  in formulæ (1) and (8) (see fig. 2a).



Since the theoretical investigation had only been carried out for the case  $p = 1/n$ , it was necessary to make sure that the velocity of the shot past the coil was such as to secure this condition. The parameters  $p$  and  $n$  are connected with the period of the galvanometer, the height of the shot above the coil, and the velocity at right angles to the coil, by the two relations  $T = 2\pi/n$  (equation 7) and  $p = d/v'$  (equation 8).

Eliminating  $p$  and  $n$  between these three equations, we have the relation

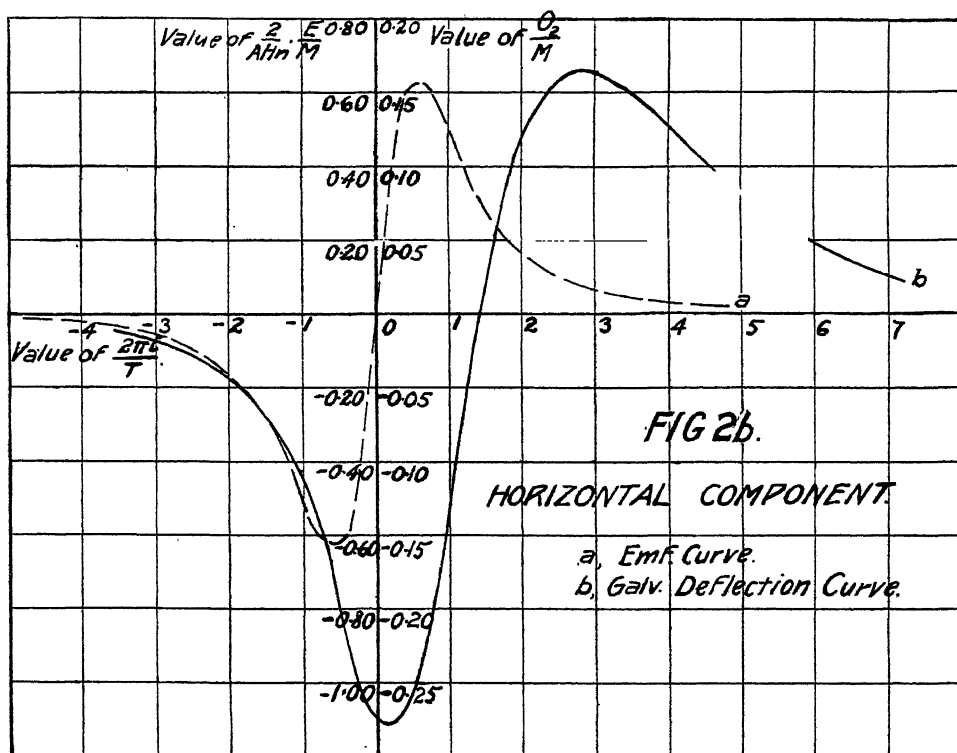
$$v' = 2\pi d/T, \quad (13)$$

which gives the required velocity.

Plate 1a gives a record of the galvanometer deflection in this case for  $d = 14.6$  cm. The thick black line is the deflection record, the thin grey lines on either side being only ghosts. The deflection agrees very well with the curve of fig. 2a, although the shot velocity was a little low, 10.2 cm. per second instead of 11.6. The maximum deflection measured on the record is 17.0 mm., which is in fair agreement with 14.3 mm., the deflection calculated from formula (12). The difference is probably due to slight permanent magnetisation of the shell.

With the coil in a horizontal position, trouble was experienced at first, due to large disturbances presumably caused by induction from the tramways in the neighbourhood. These disturbances were completely cut down by connecting in series with the coil, and in opposition to it, three turns of wire laid round the laboratory, and enclosing a total area equal to that of all the turns in the coil.

B. *Horizontal Component*.—In this case the coil was placed in a vertical

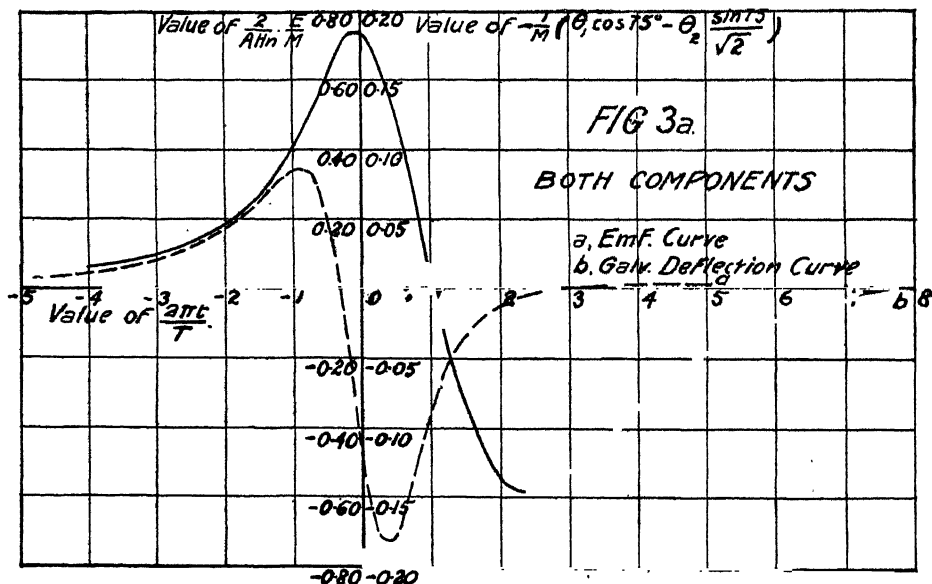


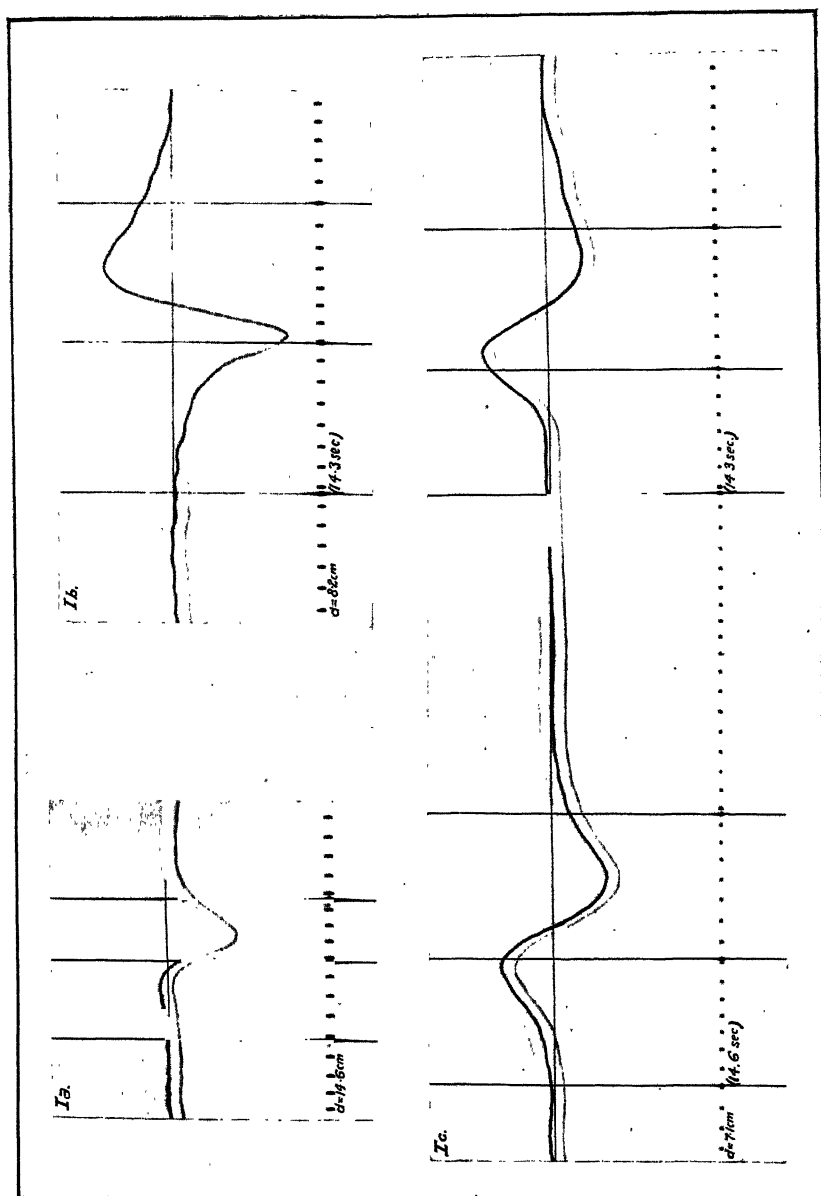


plane pointing magnetic-north and south, and the shot was moved up and down past one of its horizontal sides. The horizontal component of the earth's field was directed along the side of the coil, and the vertical component, acting along the direction of motion of the shot, played the part of a virtual horizontal component. This corresponds to  $l = \sin \delta = \sin 75^\circ$  and  $m = 0$  in formulæ (1) and (8) (see fig. 2b).

Here, again, the velocity was determined by means of formula (13). No noticeable tramway disturbances were observed in this position of the coil. Plate 1b gives a record of the galvanometer deflection for  $d = 8.2$  cm. There is good agreement with the calculated deflection shown in fig. 2b, although the velocity of the shot was somewhat low. The maximum deflection is 35 mm., against 32.2 mm. calculated from formula (12).

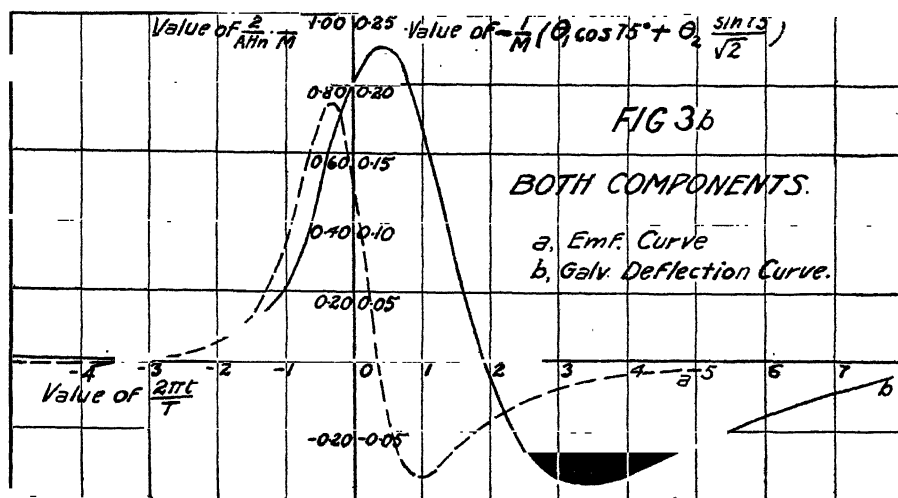
C. *Both Components Combined.*—The coil was again placed in a vertical position, but pointing in a magnetic east and west direction, with its sides inclined at  $45^\circ$  to the horizontal. Here,  $l = \sin \delta / \sqrt{2} = \sin 75^\circ / \sqrt{2}$ ,  $m = \cos \delta$ . As may be seen from equation (1), the E.M.F. due to the component parallel to the direction of motion of the shot changes sign with  $x$ , whereas that due to the component perpendicular to both the side of the coil and the direction of motion does not. The form of the E.M.F. curve and of the deflection curve will thus depend on the direction of motion of the shot. This is illustrated by the curves of fig. 3 and the record of Plate 1c. In fig. 3a, and the first deflection in the plate, the positive maximum comes just before the zero-line, and is approximately equal to the negative maximum.







In fig. 3b, and the second deflection in the plate, the positive maximum comes just before the zero-line, and is over twice the negative maximum.



#### CONCLUSION.

We have now shown that the theory agrees with experimental evidence, and we may draw further conclusions as to the way in which the galvanometer deflection varies with different factors.

The galvanometer deflection is proportional to a factor,  $M$ , given by

$$M = \frac{4nF\lambda}{AHv'} = 2 \cdot \frac{2}{AHn} \cdot F \cdot \lambda \cdot \frac{1}{d} \cdot \frac{2\pi}{T}.$$

Thus, if the velocity is that given by  $v' = 2\pi d/T$  (equation 13), the deflection will be proportional to—

- (a) The voltage sensitivity,  $2/AHn$ , of the galvanometer;
- (b) The earth's field,  $F$ ; and
- (c) The constant  $\lambda$ , which depends on the amount and distribution of magnetic material in the shell,

and will be inversely proportional to—

- (a) The depth  $d$  of the conductor below the level of the shell; and
- (b) The period  $T$  of the galvanometer.

Further, it has been found experimentally, and pointed out in the case of Plate 1,  $a$  and  $b$ , that a small variation in the velocity produces only a small effect on the deflection. The above results will therefore hold approximately even when the velocity is not that given by equation (13).

The theory also throws light upon the connection that may be expected between the deflection of a critically damped galvanometer, and the E.M.F.

variation which caused it. Two points appear at once on examination of the theoretical curves of figs. 2 and 3 :—

(a) The galvanometer deflection does not give a perfectly faithful, but a slightly distorted, reproduction of the E.M.F. curve.

(b) The galvanometer deflection lags behind the E.M.F. by an amount here equal to about one-fourth of the period.

Both these deviations from a true representation of the E.M.F. variation are due to the effect of the inertia of the moving system of the galvanometer.

*On some New Formulæ for the Numerical Calculation of the  
Mutual Induction of Coaxial Circles.*

By LOUIS V. KING, D.Sc., Macdonald Professor of Physics, McGill  
University, Montreal.

(Communicated by Prof. A. S. Eve, F.R.S. Received April 13, 1921.)

SECTION 1.—*Note on the Direct Numerical Calculation of Elliptic Integrals.*

The importance of realising rapid and accurate methods of calculating the elliptic integrals, now denoted by

$$F(\phi, k) = \int_0^\phi d\phi / \Delta(\phi, k), \quad E(\phi, k) = \int_0^\phi \Delta(\phi, k) d\phi, \quad (1)$$

where

$$\Delta(\phi, k) = \sqrt{1 - k^2 \sin^2 \phi},$$

was first remarked by Euler\* (1766), although it was not until several years later that Landen† (1775) discovered in geometrical form the transformation which forms the basis of existing methods of numerical calculation of the elliptic integrals.

A method of successive transformations for the ultimate reduction of the algebraic forms of the elliptic integrals to elementary forms was published by Lagrange‡ in 1784-5. This memoir contains an exposition of the scales of arithmetico-geometrical means and discusses their use in calculating the

\* Euler, 'Novi Comm. Acad. Sc. Petrop.', vol. 10 (1766).

† Landen, 'Phil. Trans. Roy. Soc.', vol. 65, p. 283 (1775); also, 'Mathematical Memoirs,' London, 1780.

‡ Lagrange, "Sur une nouvelle méthode de calcul intégral pour les différentielles affectées d'un radical carré sous lequel la variable ne passe pas le quatrième degré," 'Mém. de l'Acad. Roy. des Sc. de Turin,' vol. 2 (1784-5); 'Œuvres,' vol. 2, pp. 253-312 (Gauthier-Villars, Paris, 1868).

elliptic integrals of the first and second kinds in a manner practically identical with that formulated about the same time by Legendre.\*

This method, discovered independently by Gauss and called by him the "algorithm of the arithmetico-geometrical mean," originated in connection with the evaluation of complete elliptic integrals arising from a problem in attractions occurring in the planetary theory.† In a note he mentions that the results were obtained by him as part of a more comprehensive theory independently of the results of Lagrange and Legendre, with which they are closely connected.

Much use was made of the scales of arithmetico-geometrical means in the numerical calculation of elliptical integrals by Jacobi,‡ who, however, adapted his formulæ to computation by logarithms. The use of modern calculating machines has greatly extended the scope of direct numerical calculation of elliptic integrals by the methods just referred to. In many practical applications it is advantageous to have available a direct method of computation independent of auxiliary tables, the use of which often requires tedious and somewhat uncertain interpolations when seven or more significant figures are desired. Many formulæ involving elliptic functions arising in mathematical physics, when expressed directly in terms of quantities arising from the arithmetico-geometrical scales, give rise to extremely convenient expressions for direct numerical computation when a calculating machine is available.

## SECTION 2.—The Scale of Arithmetico-geometrical Means.

In forming the scale of arithmetico-geometrical means, we start with the positive numbers,  $a_0 = 1$ ,  $b_0 = k'$ ,  $c_0 = k$ ,  $k$  being the modulus of formula (1), and  $k'$  the complementary modulus,  $k'^2 = 1 - k^2$ . We calculate successively

$$\left. \begin{array}{lll} a_0 = 1, & b_0 = k', & c_0 = k \\ a_1 = \frac{1}{2}(a_0 + b_0) & b_1 = \sqrt{a_0 b_0}, & c_1 = \frac{1}{2}(a_0 - b_0) \\ a_2 = \frac{1}{2}(a_1 + b_1) & b_2 = \sqrt{a_1 b_1}, & c_2 = \frac{1}{2}(a_1 - b_1) \\ \dots\dots & \dots\dots & \dots\dots \\ a_n = \frac{1}{2}(a_{n-1} + b_{n-1}), & b_n = \sqrt{a_{n-1} b_{n-1}}, & c_n = \frac{1}{2}(a_{n-1} - b_{n-1}) \\ \dots\dots & \dots\dots & \dots\dots \end{array} \right\} \quad (2)$$

\* Legendre, "Mémoire sur les intégrations par arcs d'ellipse,"—"Second mémoire, etc.," 'Mém. de l'Acad. des Sciences de Paris, année 1786,' pp. 616-643 (Paris, 1788); also pp. 644-683; 'Traité des Fonctions Elliptiques,' vol. 1, pp. 79 *et seq.* (Paris, 1825).

† Gauss, "Determinatio Attractionis, etc.," 'Comm. Gott. Soc. Reg. Scient.,' vol. 4, 1818; 'Werke,' vol. 3, pp. 331-355 (Göttingen, 1866). The note mentioned above is dated February 9, 1818; 'Werke,' vol. 3, pp. 357-360.

‡ Jacobi, 'Fundamenta Nova,' §§ 38 and 52 (1829); 'Ges. Werke,' vol. 1, pp. 154 and 203 (Berlin, 1881); also, "Numerische Berechnung der Elliptischen Functionen," 'Crelle,' vol. 26, pp. 93-114; 'Ges. Werke,' vol. 1, pp. 345-368 (1881).

The following relations are easily verified—

$$\left. \begin{aligned} c_n^2 &= a_n^2 - b_n^2, & a_n c_n &= \frac{1}{2} c_{n-1}^2 \\ a_{n+1} + c_{n+1} &= a_n, & a_{n+1} - c_{n+1} &= b_n \end{aligned} \right\}. \quad (3)$$

The array of numbers (2) will be briefly referred to as the A.G.M. scale ( $a_0 = 1, b_0 = k'$ ). The successive  $a$ 's and  $b$ 's converge with extraordinary rapidity to the same limit, which Gauss denoted by  $M(a_0, b_0)$ . It is easily seen that

$$M(\epsilon a_0, \epsilon b_0) = \epsilon M(a_0, b_0). \quad (4)$$

The limit  $M(a_0, b_0)$  will be denoted by  $a_\infty$ , as long as by so doing no ambiguity is involved.

The following expressions for the complete elliptic integrals in terms of the A.G.M. scale ( $a_0 = 1, b_0 = k'$ ) are well known.

$$K = \frac{1}{2} \pi / a_\infty, \quad (5)$$

$$(K - E)/K = \frac{1}{2} (c_0^2 + 2c_1^2 + 4c_2^2 + \dots + 2^n c_n^2 + \dots). \quad (6)$$

It does not appear to have been remarked hitherto that  $2^{-n} \log(a_n/c_n)$  also converges rapidly to a definite limit which enables us to compute the complementary integrals  $K'$ ,  $E'$ , and the nome  $q$  given by  $\log q = -\pi K/K'$ .

It may be proved\* that

$$\frac{1}{2} \pi a_n / a_n' = \frac{1}{2} \pi K' / K = 2^{-n} \log(a_n / c_n). \quad (7)$$

More convenient for calculation is the following formula, derived from (7) and the relations (3)

$$\log(1/q) = \pi K' / K = \log(4a_1/c_1) - \sum_1^\infty \left(\frac{1}{2}\right)^{n-1} \log(a_n/a_{n+1}). \quad (8)$$

Making use of Legendre's relation,

$$E/K + E'/K' - 1 = \frac{1}{2} \pi / (KK'), \quad (9)$$

we easily derive the series

$$\begin{aligned} K' - E' &= \frac{1}{2} a_n \left( \log \frac{4a_1}{c_1} - \log \frac{a_1}{a_2} - \frac{1}{2} \log \frac{a_2}{a_3} - \dots \right) \\ &\quad (1 - \frac{1}{2} c_0^2 - c_1^2 - 2c_2^2 - 4c_3^2 - \dots) - a_n. \end{aligned} \quad (10)$$

\* The proof will be given in a memoir on the numerical calculation of elliptic functions which the writer has in preparation. The writer has been unable to find this formula explicitly stated by Gauss or by any subsequent writer on elliptic functions. It furnishes the key, however, to many remarkable formulæ found among Gauss's unpublished papers, stated without proofs ('Werke,' vol. 3 (1866)); Nachlass, 'Arithmetisch-Geometrisches Mittel,' pp. 361-402; also, 'Zur Theorie der Neuen Transcendenten,' pp. 446 *et seq.* The series (8) is, however, given without proof by Gauss (*loc. cit.*, p. 377), who may have been in possession of (7), but for some reason disposed to withhold the publication of this key-formula.

SECTION 3.—Application to Mutual Inductance Formulæ for Coaxial Circles.

Let  $A$  be the radius of the larger circle,  $a$  that of the smaller, and  $d$  the distance between their planes. We also denote by  $r_1$  and  $r_2$  the greatest and least distances respectively of a point on one circle to the circumference of the other. Maxwell\* derived two well-known formulæ for  $M$ , the coefficient of mutual induction of the two circles;

$$\left. \begin{array}{l} \text{where} \quad M = 8\pi (K/k) \sqrt{(Aa)} [1 - E/K - \frac{1}{2} k^2] \\ \text{and} \quad k^2 = 4Aa / \{(a+A)^2 + d^2\}, \quad k' = r_2/r_1 \\ r_1^2 = (A+a)^2 + d^2, \quad r_2^2 = (A-a)^2 + d^2 \end{array} \right\} \quad (11)$$

Landen's transformation applied to (11) gives rise to Maxwell's second formula

$$M = 8\pi \sqrt{(Aa/k_1)} (K_1 - E_1), \quad (12)$$

where  $K_1$  and  $E_1$  are the complete elliptic integrals to modulus

$$k_1 = (r_1 - r_2)/(r_1 + r_2). \quad (13)$$

If we compute the A.G.M. scale ( $a_0 = r_1$ ,  $b_0 = r_2$ ), it is readily proved from (4), (5), and (6) that both (11) and (12) give rise to

$$M = \{2\pi^2/a_n\} [c_1^2 + 2c_2^2 + 4c_3^2 + \dots + 2^{n-1}c_n^2 + \dots], \quad (14)$$

a most convenient and elegant formula for the direct computation of  $M$ .

This series is always extremely convergent, since from (7) the successive values of  $c$  tend to converge like the series

$$x \quad x^2 \quad x^4 \quad x^8 \quad x^{16} \dots x^{2^n} \dots \quad \text{where } x < 1.$$

When the circles are *very close together*,  $k'$  is small and it is more convenient to use the *complementary* A.G.M. scale, which is then extremely convergent. The first few terms are as follows:—

$$\left. \begin{array}{cccc} n & a_n' & b_n' & c_n' \\ 0 & r_1 + r_2 & r_1 - r_2 & 2\sqrt{(r_1 r_2)} \\ 1 & r_1 & 2\sqrt{(Aa)} & r_2 \\ 2 & \frac{1}{2} r_1 + \sqrt{(Aa)} & (4Aar_1^2)^{\frac{1}{2}} & \frac{1}{2} r_1 - \sqrt{(Aa)} \end{array} \right\} \quad (15)$$

Making use of (10) and (12), we easily obtain the following formula for  $M$  in terms of the complementary A.G.M. scale (denoted by accented letters):—

$$M = 2\pi a_n' \left[ \frac{(r_1'^2 - 2c_2'^2 - 4c_3'^2 - \dots)}{a_n'^2} \left( \log \frac{4a_2'}{r_2} - \frac{1}{2} \log \frac{a_2'}{a_3'} - \frac{1}{4} \log \frac{a_3'}{a_4'} - \dots \right) - 2 \right]. \quad (16)$$

Logarithms to the base 10 may be used in computing the second series,

\* Maxwell, 'Electricity and Magnetism,' 3rd ed., sec. 701 (1904).



which may finally be multiplied by the factor  $\mu = \log_e 10 = 2.30258509$  to convert to logarithms to base  $e$ .

For accuracy the first term of the above formula should exceed twice the second term. This will be the case if  $r_1/r_2 > 13$ , about. Hence formula (16) is suitable for computation when the circles are so close together that  $r_2/r_1 < 0.1$ . It may, without serious loss of accuracy, be extended to cases where  $r_2/r_1 < 0.2$ , in which case seven-figure accuracy only requires the complementary A.G.M. scale (15) to be computed as far as  $n = 2$ .

The formula (14) is, however, so much simpler than (16) that it may be used even when the circles are very close together. It has the advantage of depending only on figures derived by direct computation on a calculating machine, and does not depend on the use of logarithmic tables.

By dividing up coils of finite cross-section into a number of coils of sufficiently small cross-section, we may make use of a formula of quadratures for computing the mutual induction, depending on the calculation of the coefficients for the elementary coils taken in pairs. For this purpose the simple formula (14) is specially applicable, while (16) may be useful in some cases. Extremely convergent formulæ for the numerical computation of the induction coefficients of coaxial single-layer coils may be obtained by the use of A.G.M. scales and trigonometrical recurrence-formulæ. These depend on a number of new formulæ for the computation of the incomplete elliptic integrals of the first, second, and third kinds, which it is hoped to deal with in a future paper.

#### SECTION 4.—*Numerical Illustrations.*

To illustrate the rapid convergence of the A.G.M. scales, Gauss\* works out an example, starting with  $a_0 = 1$ ,  $b_0 = 0.2$ , and finds that  $a_5$  and  $b_5$  are represented by the same number to fifteen significant figures.

The usual arithmetical process of extracting square roots is easily adapted to calculating machines of modern construction.† In carrying out the computations, the work is considerably shortened by keeping in mind the rule that if the first  $p$  out of the  $n$  digits of the number required in the square root have been obtained by the usual process, the next  $(p-1)$  digits can be obtained by division only, with a possible error of 1 in the last digit.‡

The following numerical examples, taken from the collection of formulæ

\* Gauss, 'Werke,' vol. 3, p. 363 (1866).

† A description of modern calculating machines is given by Horsburgh, E. M., 'Modern Instruments and Methods of Calculation' (London, G. Bell and Sons, 1914); also by d'Ocagne, 'Le Calcul Simplifié' (Gauthier-Villars, Paris, 1905).

‡ Chrystal's 'Algebra,' Part I, 5th ed., p. 210 (1904)

published by the Washington Bureau of Standards,\* illustrate the advantages of formulæ (14) and (16) in numerical computation.

*Example 1.* 'Bulletin 169,' p. 32 (1916). *Equal circles at a distance.*

$A = a = 25$  cm.,  $d = 50$  cm.,  $r_1 = 50\sqrt{2}$  cm.,  $r_2 = 50$  cm.

$n$ .	$a_n$ .	$b_n$ .	$c_n$ .	$c_n^2$ .
0	70·71067812	50·00000000	—	—
1	60·35533909	59·46035575	10·35533906	107·23804776 <sub>1</sub>
2	59·90784740	59·90617607	0·44749167	0·20024879 <sub>5</sub>
3	59·90701174	59·90701173	0·00083567	0·00000069 <sub>8</sub>

To an order of accuracy of ten significant figures, we need take only three terms of (14), which then gives, with  $2\pi^2 = 19\cdot7392088022$ ,

$$M = \frac{2\pi^2}{a_4} (c_1^2 + 2c_2^2 + 4c_3^2) = \frac{2\pi^2 \times 107\cdot63354814_3}{59\cdot90701173_5} = 35\cdot46498187_8 \text{ cm.}$$

It is readily seen that little additional labour is involved in carrying out the computations to ten significant figures. Values quoted in the above-mentioned 'Bulletin 169,' computed by three different formulæ expressed in  $q$ -series, derived by Nagaoka, give for  $M$  the three values

$$35\cdot464975 \text{ cm.,} \quad 35\cdot464981 \text{ cm.,} \quad 35\cdot46481 \text{ cm.}$$

In carrying out the computation, there is no need to write down more figures than are set down above, all the processes being carried out on the calculating machine.

*Example 2.* 'Bulletin 169,' pp. 21, 22, 28 (1916). *Equal circles close together.*

$A = a = 25$  cm.,  $d = 1$  cm.,  $r_1 = 50\cdot010000$ .  $r_2 = 1\cdot00000000$ .

From (15) we write down the complementary A.G.M. scale—

$n$ .	$a'_n$ .	$b'_n$ .	$c'_n$ .
1	50·010000	50·000000	1·000000
2	50·005000	50·005000	0·005000

Formula (16) then gives to eight significant figures.

$$M = 2\pi \left[ \left( \frac{r_1^2 - 2c_2'^2}{a_3'} \right) \log \frac{4a_2'}{r_2} - 2a_3' \right] \\ = 2\pi \left[ \frac{2501\cdot0000}{50\cdot005000} \times \log (200\cdot02000) - 100\cdot01000 \right],$$

$$\text{or} \quad M = \pi \left[ \frac{1000\cdot4000}{5\cdot2984174} - 200\cdot0200 \right] = 1036\cdot6648_2 \text{ cm.}$$

\* Bulletin 169, 'Formulas and Tables for the Calculation of Mutual and Self-Inductance,' by Rosa and Grover, 3rd ed., 1916.

## 66 Calculation of the Mutual Induction of Coaxial Circles.

Values derived from Legendre's tables and two series formulæ are given as

$$1036\cdot6664 \text{ cm.}, \quad 1036\cdot6652 \text{ cm.}, \quad 1036\cdot663 \text{ cm.}$$

A comparison of the numerical work involved emphasises in marked manner the advantage of the new formula (16).

It is interesting to check this result by formula (14), although the present example is not favourable to its use.

The computation proceeds as follows:—

$n.$	$a_n.$	$b_n.$	$c_n.$	$c_n^2.$
0	50·01000 <sub>0</sub>	1·00000 <sub>0</sub>	—	—
1	25·50500 <sub>0</sub>	7·07177 <sub>4</sub>	24·50500	600·4950
2	16·28833 <sub>7</sub>	13·43000 <sub>0</sub>	9·21661	84·9459
3	14·85919 <sub>3</sub>	14·79080	1·42919	2·0426
4	14·82475	14·82471	0·03445	0·0012
5	14·82473	14·82473	0·00002	0·0000

Even in this unfavourable case, four terms of (14) are more than sufficient to give an accuracy to seven significant figures, and

$$M = \frac{2\pi^2}{a_5} (c_1^2 + 2c_2^2 + 4c_3^2 + 8c_4^2) = \frac{2\pi^2 \times 778\cdot5666}{14\cdot82473} = 1036\cdot666 \text{ cm.}$$

The labour of computation by the above formula is still less than that involved in the use of Legendre's Tables or of any of the series formulæ.

### SECTION 5.—*Summary and Conclusions.*

The use of the modern calculating machine for the extraction of square roots makes the *scales of arithmetico-geometrical means* extremely convenient for the direct and rapid computation of the complete elliptic integrals.

This procedure is applied to Maxwell's formulæ for the coefficient of mutual induction of coaxial circles, with the result that two new and elegant formulæ are obtained for numerical computation.

Numerical examples, taken from the well-known collection of formulæ and tables for the calculation of self and mutual induction, issued by the Bureau of Standards, illustrate the advantage of the new formulæ in economy of labour.

*Gaseous Combustion at High Pressures. Part II.—The Explosion of Hydrogen-Air and Carbon Monoxide-Air Mixtures.*

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S., and the late WILLIAM ARTHUR HAWARD, M.Sc., Salters' Research Fellow.\*

(Received June 14, 1921.)

*Introduction.*

In a previous paper upon the subject,† the question was propounded whether or no there is any direct relation between the actual rate at which the potential energy of an explosive mixture is transferred on explosion as sensible heat to its products and the magnitude of the chemical affinity between its combining constituents. As the result of an experimental enquiry into the matter, it was proved:—

(a) that, whereas the affinity for oxygen of methane is at least twenty to thirty times greater than that of hydrogen, the time required for the attainment of maximum pressure in the case of the primary methane-air mixture ( $\text{CH}_4 + \text{O}_2 + 4\text{N}_2$ ) is at least some five to eight times as long as that required in the case of the primary hydrogen-air mixture ( $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ );

(b) that whereas in mixtures corresponding to  $\text{CH}_4 + \text{O}_2 + x\text{H}_2$  (in which  $x$  was varied between 2 and 8), the "mass influence" of successive increases in  $x$  upon the actual oxygen distribution between the two combustible gases is proportional to  $x^2$ , yet in mixtures corresponding to  $\text{CH}_4 + \text{O}_2 + x\text{CO}$  it is nearly proportional to  $x$ ; or, in other words, whilst the "mass influence" of hydrogen is proportional to the square, that of carbon monoxide is in accordance with the first power, of its concentration;

(c) that in hydrogen-air and carbon monoxide-air mixtures corresponding to  $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$  and  $2\text{CO} + \text{O}_2 + 4\text{N}_2$ , respectively, in which the com-

\* This paper had been drafted for communication to the Royal Society only a few days before the occurrence of the accident in my laboratory (December 6, 1920) which so tragically ended poor Haward's life. He was suddenly struck down by death whilst actually engaged upon some final experiments designed to test and develop some of the theoretical issues set forth in the concluding paragraphs. This further part of the work will have to be completed by other hands than his, now that the apparatus has been overhauled and its damaged parts made good. Meanwhile, Haward's experimental results are being published in practically the same form as he last reviewed them with me, not only because of their exceptional interest, but also as a tribute to his great experimental skill and passionate devotion to scientific research. He laid down his life in the cause of science at the age of 26 years. A short sketch of his distinguished career appeared in 'Nature,' on December 16, 1920.—W. A. B.

† W. A. Bone and others, 'Phil. Trans.,' A, vol. 215, p. 275.

bustible gas and oxygen are present in their combining proportions, and which on explosion develop practically the same total energy (equivalent to 68.4 K.C.U. per gram-molecule in the case of hydrogen, and 68.0 in the case of carbon monoxide), the time taken for the attainment of the maximum pressure on explosion is at least ten times longer in the case of carbon monoxide than in that of hydrogen.

It thus appeared that the rate at which the potential energy of an explosive mixture is transferred into thermal energy, as measured by the rise in pressure when the explosion is carried out in a closed vessel, is not primarily determined by the chemical affinity between the combustible gas and oxygen, as ordinarily understood, but by some other factor or circumstance, then unknown, and which, therefore, required closer investigation. The present paper embodies the results of further experiments upon the matter.

### *Experimental.*

*Apparatus and Experimental Method.*—The apparatus and methods employed in these further experiments have been substantially the same as those already described in the previous paper.\* Seeing, however, that it was now desired always to obtain optical records of the complete pressure curves on exploding the various experimental mixtures, we employed throughout the spherical bomb B,† to which was attached the Petavel recording manometer with its optical accessories.‡ The bomb had a spherical cavity 3 inches in diameter (capacity approximately 275 c.c.), which, when fitted with its coned admission valve, ignition plug, and the Petavel manometer, was easily capable of holding up a pressure of 600 atmospheres. The reader is referred to the former paper for details concerning (a) the mode of admitting and mixing the various constituents of the gaseous mixture at the outset of each experiment, (b) the ignition device, and (c) the optical recording of the pressure during the explosion which followed. An electrically controlled tuning-fork, giving 100 vibrations per second, was employed as a time indicator, the fork being so placed that each vibration momentarily interrupted the light falling on to the photographic film of the pressure-recording apparatus, thus producing a dotted instead of a continuous pressure curve. We were thus able to measure the time taken in each experiment for the attainment of maximum pressure to within 0.005 second, but not much closer, which however, was sufficiently

\* *Loc. cit.*, pp. 276–287 and 314–15.

† *Loc. cit.*, figs. 5 and 6.

‡ *Loc. cit.*, figs. 14 and 15.

accurate for our purpose.\* Certain minor improvements made in the optical arrangements since the previous research enabled us to obtain even better pressure records, which could therefore be read and measured with somewhat greater accuracy than before. The ratio of the *maximum* to the *initial* pressure could usually be determined to within about 1 per cent. of the true value, or, say, to the first decimal place.

The substantial purity of the gases employed for making the various experimental mixtures was in each case always established by chemical analysis. The nitrogen and hydrogen used had been bought from trustworthy sources in cylinders under 100 atmospheres pressure. The carbon monoxide and oxygen were prepared in the laboratory (by methods already described in the previous paper),† and then compressed on the spot into cylinders up to 100 atmospheres before use.

Altogether fifty-two experimental mixtures, the exact composition of which was subsequently determined by analysis, were exploded in the bomb, each at an initial pressure of 50 atmospheres. The results of the first twenty were, however, discarded as being somewhat less reliable than the rest; because of a suspicion that in some of them there might have been a slight lag in the rising pressure curve due to a possible sticking of the moving parts of the Petavel manometer, which was thereupon thoroughly cleaned and overhauled. With one or two exceptions, the records obtained in the remaining thirty-two experiments, when the manometer was working at its maximum sensitiveness, were all remarkably clear and concordant; the results of some eighteen of them were finally selected for the purpose of this paper.

During the course of the research, the tightness of the bomb, and the condition of the surface of its explosion chamber, were frequently tested by exploding in it mixtures of oxygen with excess of hydrogen. This precaution was always necessary after any experiment in which (as was sometimes the case) an experimental mixture containing an excess of oxygen had been exploded, with consequent possible slight oxidation of the walls of the explosion chamber. Such experiments were, therefore, always followed by a

\* In amplification of this statement, it may be explained that the recording apparatus enabled us to measure quite definitely 0.005 sec., which in most of the experiments was less (and in some considerably so) than the time actually taken to attain the maximum pressure. And in such cases the record of the pressure curve obtained was invariably a line free from any sign of "vibration" either in passing through or after attaining the maximum point. On the other hand, in one or two experiments, in which the maximum pressure was attained in less than 0.005 sec., the record showed some sign of such vibration just after the maximum had been reached.

† *Loc. cit.*, p. 277.

series of oxygen with excess hydrogen explosions, until the resulting contraction was observed to be exactly equal to three times the partial pressure of the oxygen originally taken.

More than forty optical calibrations were made of the Petavel manometer during the research, from which the various optical explosion pressure records were subsequently gauged.

It was assumed that any slight deviation of the four diatomic gases, hydrogen, carbon monoxide, nitrogen, and oxygen, from Boyle's law, within the experimental condition, might be considered as negligible for all practical purposes; and actual trials in the bomb of the compressibilities of hydrogen and nitrogen, respectively, confirmed this view. In cases where mixtures containing carbon monoxide were exploded, the observed final pressure of the cold products ( $P_f$ ) were always "corrected" for the ascertained deviation of their carbon dioxide-content from the law.

In the tabulated experimental results:—

$P_i$  = the initial pressure in atmospheres at which each mixture was fired.

$P_m$  = the maximum pressure in atmospheres attained in the explosion.

$P_f$  = the final pressure in atmospheres of the cooled products of combustion.

$P_k$  = the actual pressure in atmospheres of the real "knall-gas."

$t_m$  = time in seconds taken for the attainment of maximum pressure after ignition.

$\Sigma$  = the thermal equivalent in K.C.U. of the total energy liberated during the explosion.

1ST SERIES.—*Experiments with Mixtures*  $2H_2 + O_2 + 4X_2$  (where  $X_2 = N_2$ ,  $H_2$ , or  $O_2$ ).

In each of these experiments, the object of which was to find to what extent (if at all) the rate of attainment of maximum pressure in an hydrogen air mixture ( $2H_2 + O_2 + 4N_2$ ) would be affected by the substitution for the diluent nitrogen of an equivalent molecular proportion of hydrogen or oxygen, the original mixture was fired at an initial pressure of 50 atmospheres. It was very difficult, indeed hardly possible, always to make the mixtures of *exactly* the intended composition; but by selecting for comparison those in which the difference between the initial and final pressures of the cold mixture and products, respectively, was as nearly as possible equal to 21.4 atmospheres, any experimental error due to such cause was minimised.

The results of six typical experiments are tabulated on p. 71.

Table I.—Results of Experiments (1st Series) with  $2\text{H}_2 + \text{O}_2 + 4\text{X}_2$  Mixtures.

Experiment .....	I.	II.	III.	IV.	V.	VI.
Mixture .....	$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$			$2\text{H}_2 + \text{O}_2 + 4\text{O}_2$	$2\text{H}_2 + \text{O}_2 + 4\text{H}_2$	
Initial temp., C. ...	18·5°	17·5°	14·7°	22·5°	11·0°	11·0°
Pressures in atmos. $\left\{ \begin{array}{l} P_i \dots\dots \\ P_k \dots\dots \\ P_f \dots\dots \\ P_m \dots\dots \end{array} \right.$	50·0	50·0	50·0	50·0	50·0	50·0
	21·7	21·2	21·7	21·5	21·8	21·7
	28·8	28·5	28·3	28·8	28·2	27·5
	405	391	402	400	408	408
Ratio $P_m/P_i$ .....	8·1	7·8	8·04	8·0	8·16	8·16
$t_m$ secs. ....	0·005			about 0·010	about 0·0025	
$\Sigma$ K.C.U. ....	10·45	10·18	10·50	10·33	10·48	10·40

We succeeded in obtaining three exceptionally good records of the pressure-curves in the hydrogen-air ( $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ ) mixtures, one of which (Experiment I) is reproduced in fig. 1. They each showed an almost instantaneous rise (in about 0·005 second) to the maximum pressure of about 400 atmospheres, the attainment of which was immediately succeeded by the commencement of the cooling period. The cooling curves, however, all gave some indication of there having been a slight evolution of heat during a short period (about 0·10 second) after the actual attainment of the maximum pressure, thereafter becoming straight lines.\*

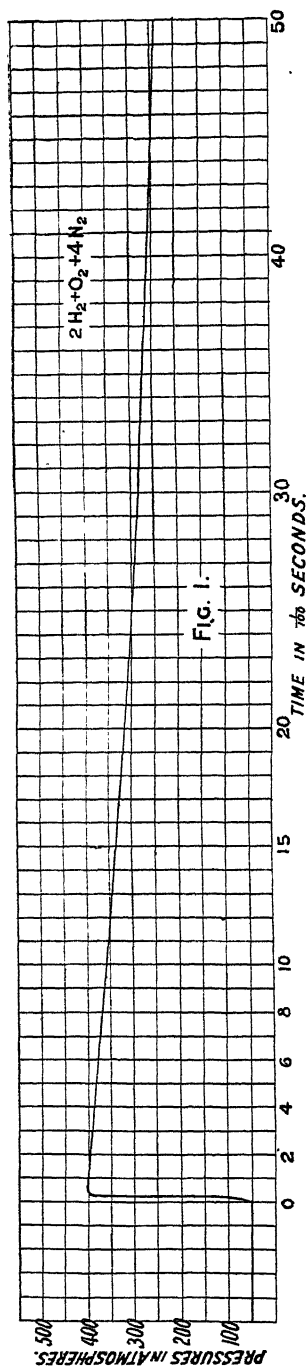
It is of interest to compare our time-pressure curve with the time-temperature curve deduced by Prof. W. T. David from his recent experiments on "Radiation in Explosions of Hydrogen and Air"† for the explosion of a mixture of nearly the same composition (a 25·4 per cent. hydrogen mixture) as ours in a closed vessel with blackened walls at atmospheric pressure. His maximum temperature (2400° C. abs.) was reached in 0·017 sec. after ignition; and his cooling curves gave no indication of any heat evolution occurring in the system after the maximum temperature had been passed. He also found that the mixture in question lost as much as 16·1 per cent. of its total potential energy (heat of combustion) by radiation, nearly the whole of which was emitted during the cooling period at a rate approximately

\* In the previous paper (*loc. cit.*, pp. 316 and 317) the time observed for the attainment of maximum pressure for similar mixtures of  $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ , when fired in the bomb at initial pressures of 50 atmospheres, was 0·010 sec., and the succeeding cooling-curve (*q.v.*) was practically a straight line throughout. This slight difference between the new and the old results is to be ascribed to the somewhat greater sensitiveness of the pressure-recording part of the apparatus in the present research than formerly.

† 'Proceedings,' A, vol. 98, p. 185 (1920).



proportional to the fourth power of the absolute temperature. It may

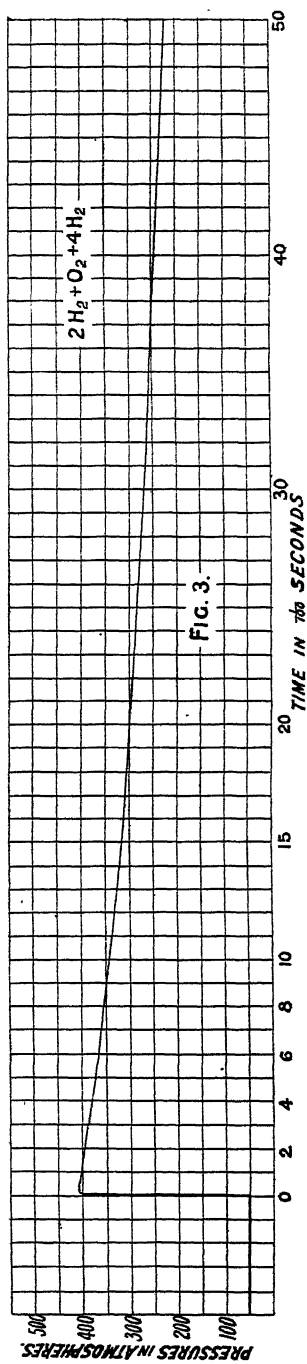
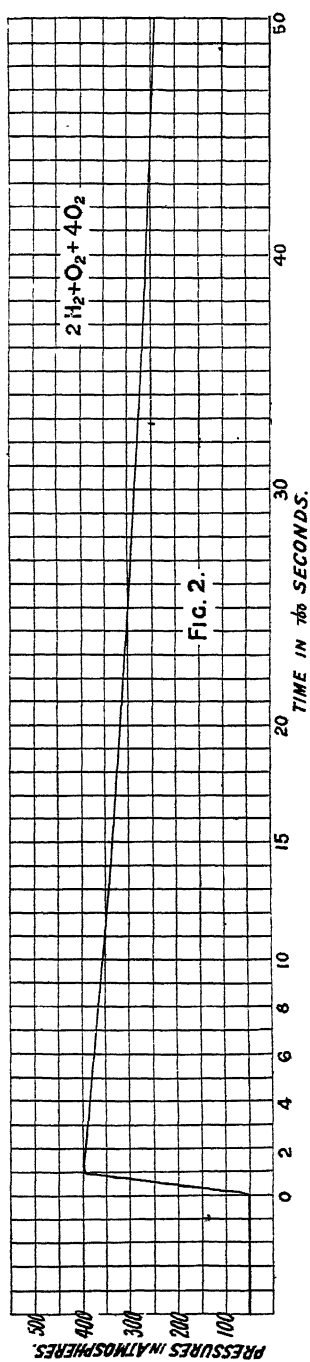


also be noted that, whereas until the temperature had fallen to  $1,200^{\circ}$  C. abs. this radiation consisted chiefly of the  $2.8\mu$  band of "steam" (as found in a hydrogen flame), at the highest temperature ( $2,400^{\circ}$  to  $2,200^{\circ}$  C. abs.) some radiation of shorter wave was emitted; also that below  $1,200^{\circ}$  C. abs. (at which the  $2.8\mu$  line had almost ceased) some of greater wave-length could be detected. The fact that the emission of radiation of shorter wave-lengths than  $2.8\mu$  has been detected at the highest temperature during hydrogen-air explosions seems to us to be of some significance in connection with the theory of combustion, suggesting, as it does, the initial transitory formation of an intensely vibratory complex when hydrogen and oxygen combine in flames, a consideration that will be referred to again in the concluding part of the paper.\*

From Table I, it will be seen that the substitution of hydrogen or oxygen for nitrogen as the diluent gas had no very marked influence upon the course of the explosion; if anything, the substitution of hydrogen quickened, and that of oxygen somewhat retarded, the attainment of the maximum pressure. Also, the substitution of hydrogen tended to quicken slightly the cooling, as, indeed, might be expected from its greater heat conductivity and mobility than nitrogen. Two typical curves, one for

\* Professor David himself rather suggested that it might be due to the presence of nitrogen in the exploded gases, because nitrogen gives a strong emission band at  $1\mu$  in a vacuum tube (*loc. cit.*, p. 192, footnote); but it may be doubted whether nitrogen would become emissive in an explosion,

and the above interpretation seems to be the better one.



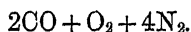
the mixture  $2\text{H}_2 + \text{O}_2 + 4\text{O}_2$  (Experiment IV), and the other for the mixture  $2\text{H}_2 + \text{O}_2 + 4\text{H}_2$  (Experiment V), are reproduced in figs. 2 and 3 respectively; and in Table II the three curves are analysed.

Table II.—Analysis of Curves shown in Figs. 1, 2 and 3.

$t$ . (secs. after ignition).	Fig. 1. Experiment I.	Fig. 2. Experiment IV.	Fig. 3. Experiment V.
	$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ .	$2\text{H}_2 + \text{O}_2 + 4\text{O}_2$ .	$2\text{H}_2 + \text{O}_2 + 4\text{H}_2$ .
	P. atmos.	P. atmos.	P. atmos.
0·000	50	50	50
0·025 to 0·010*	405	400	408
0·050	385	380	371
0·100	358	355	343
0·150	337	337	320
0·200	317	320	300
0·300	282	288	267
0·400	260	263	242
0·500	237	242	222
0·600	218	221	204
0·700	198	205	189
0·800	185	190	—
0·900	174	179	—
1·000	164	168	—

\* This represents  $t_m$ , the time taken for the attainment of  $P_m$ , which varied between 0·0025 and 0·010 sec. in the different experiments (*vide* Table I).

## 2ND SERIES.—*Experiments with Carbon Monoxide-Air Mixtures*



For comparison with the behaviour of the foregoing hydrogen-air mixtures (Experiments I to III inclusive), the following three experiments (VII to IX inclusive) with CO-air mixtures ( $2\text{CO} + \text{O}_2 + 4\text{N}_2$ ), liberating the same total amount of energy on combustion, were made. Unfortunately, the original mixture in Experiment VII was afterwards found to have been weaker ( $\text{CO} = 26\cdot35$  instead of  $28\cdot6$  per cent.), and that in Experiment IX slightly stronger ( $\text{CO} = 30\cdot1$  instead of  $28\cdot6$  per cent.) than had been intended. In Experiment VIII, however, the mixture was of exactly the right composition, and therefore its results were finally selected for detailed comparison with those of the correspondingly best experiment with the hydrogen-air mixture (Experiment I, *q.v.*). In all cases most excellent records were obtained of the pressure curves, one of which (from Experiment VIII) is reproduced in fig. 4 and analysed in detail. The results of the whole series are epitomised in Table III.

Comparing now figs. 1 and 4, it will at once be seen how strikingly dissimilar was the whole course of the combustion and subsequent cooling, although the total energy developed was as nearly as possible the same, in the two cases. In the case of the CO-air mixture (fig. 4), not only was the ratio  $P_m/P_i$  distinctly higher, but the time taken for the attainment of maximum pressure ( $t_m$ ) was about thirty-six times longer than in the corresponding experiment (fig. 1) with the  $H_2$ -air mixture. It may here be stated that there were indications that the time in question was not quite so constant in the CO-air series as it had been in the  $H_2$ -air series, being apparently influenced to some extent by the hygroscopic state of the mixture, as, indeed, might be expected from H. B. Dixon's well-known work on the combustion of carbon monoxide. It is intended, in future experiments, to investigate this particular point more fully, as it appears to be of practical interest in connection with internal combustion engine problems.

Another notable difference between the two curves in question is that, whereas in the case of the hydrogen-air mixture, the cooling commenced almost immediately after the attainment of the maximum pressure, in the case of the CO-air mixture it was delayed for quite an appreciable time interval thereafter, showing that heat energy was still being liberated long after the maximum temperature had been reached. Also, the subsequent rate of cooling after  $t_m$  was very much slower in the CO-air than in the  $H_2$ -air series. Indeed, nothing could be more strikingly different than the modes of combustion of carbon monoxide and

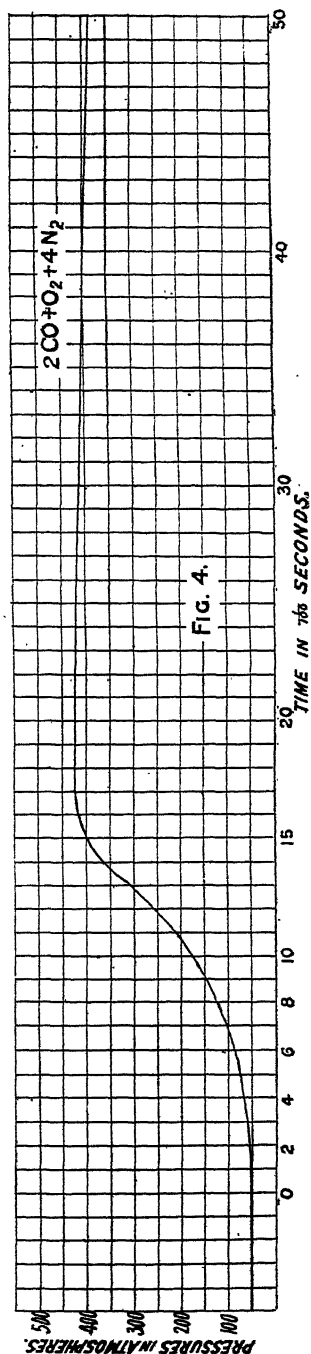


Table III.—Results of Experiments (2nd Series) with  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  Mixtures.

Experiment .....	VII.	VIII.	IX.
Per cent. CO in the mixture .....	26·35	28·6	30·1
Initial temp., C. ....	16·5°	18·2°	18·5°
Pressures in atmos. $\left\{ \begin{array}{l} P_i \\ P_k \\ P_f \text{ (corrected)} \\ P_m \end{array} \right.$ .....	50·00	50·00	50·00
	19·75	21·45	22·50
	41·80	41·50	41·66
	378	421	410
Ratio $P_m/P_i$ .....	7·56	8·42	8·2
$t_m$ secs. ....	0·24	0·18	0·19
$\pm$ K.C.U. ....	9·43	10·23	10·78

hydrogen as revealed by these two curves. An analysis of the CO-air curve (fig. 4) is given below:—

Analysis of CO-Air Pressure Curve. (Fig. 4.)

Time (secs.) after ignition	0·00	0·05	0·10	0·15	0·18	0·20	0·25
Pressure (atmos.) .....	50	76	173	398	421	421	416
Time (secs.) after ignition	0·30	0·40	0·50	0·60	0·70	0·80	0·90
Pressure (atmos.) .....	412	395	383	373	362	352	342
							1·00
							332

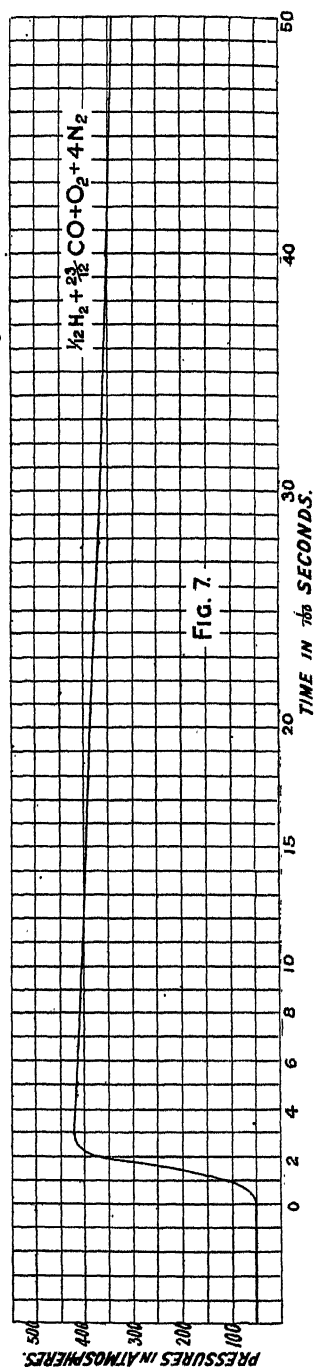
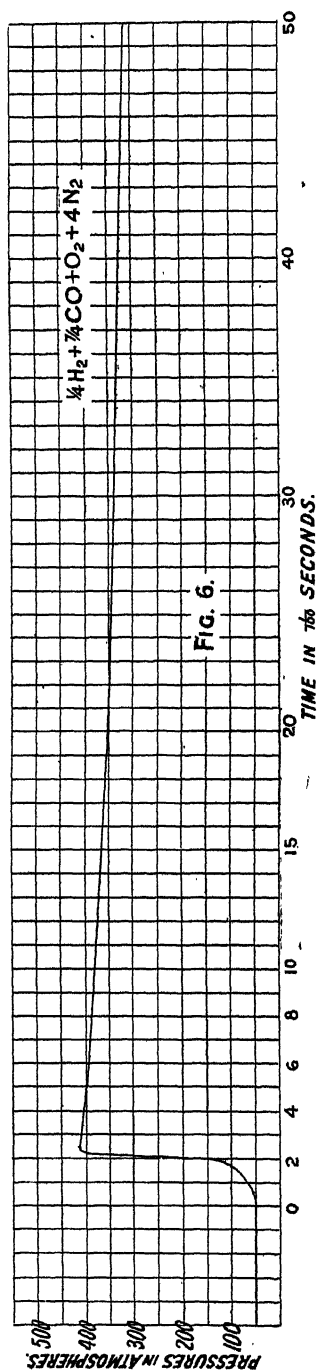
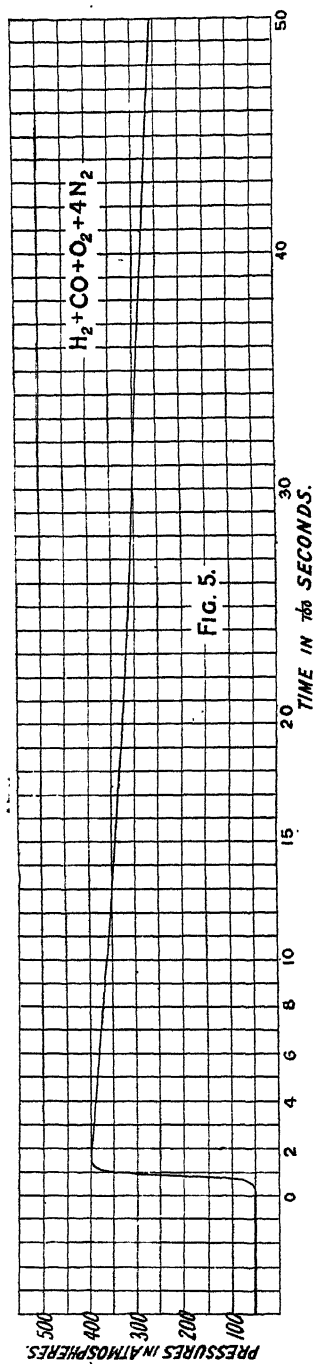
Indeed, a detailed comparison between the results of the two sets of Experiments I to IV (with  $\text{H}_2$ -air mixtures) and VII to IX (with CO-air mixtures) respectively, has shown that, in the latter, not only was there always an interval of about 0·05 second, during which the maximum pressure was fully maintained, but also, subsequently, the pressure fell at only half the rate it had done in the former.

### 3RD SERIES.—*Experiments with Isothermic Mixtures* $2(m\text{H}_2 + n\text{CO}) + \text{O}_2 + 4\text{N}_2$ .

It now seemed important to determine whether or not the marked disparity observed in the preceding series of experiments between the rates of attainment of maximum pressure in the  $\text{H}_2$ -air and CO-air mixtures, respectively, can be ascribed to some difference in the molecular properties of the two combustible gases concerned. If so, then their separate influences upon the rate of attainment of maximum pressure should be *additive* when isothermic mixtures  $2(m\text{H}_2 + n\text{CO}) + \text{O}_2 + 4\text{N}_2$  (where  $m$  and  $n$  are variable,

TABLE IV.  
Results of Experiments (3rd Series) with Isothermic Mixtures  $2(m\text{H}_2 + n\text{CO}) + \text{O}_2 + 4\text{N}_2$ .

Exp't.	Approximate mixture.	Percentage composition of the mixture				Initial temperature, C.	Pressures in atmos.		Ratio $P_m/P_r$ .	$t_m$ (secs.) observed.	$t_m$ (secs.) calculated on supposition of additive effects.	$\Sigma$ K.C.U.
		CO.	H <sub>2</sub> .	O <sub>2</sub> .	N <sub>2</sub> .		P <sub>r</sub> .	P <sub>m</sub> .				
II	$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ .....	Nil	28.20	14.50	57.30	17.5	50	391	7.82	0.005	—	10.18
X	$\left\{ \begin{array}{l} \text{H}_2 + \text{CO} + \text{O}_2 + 4\text{N}_2 \dots\dots \end{array} \right\}$	14.5	13.0	15.1	57.4	20.5	50	399	7.98	0.015	0.092	9.87
XI		13.65	13.85	14.90	57.60	20.4	50	390	7.80			
XII	$\frac{1}{3}\text{H}_2 + \frac{2}{3}\text{CO} + \text{O}_2 + 4\text{N}_2$ .....	19.90	6.70	14.55	58.85	21.5	50	410	8.2	0.015	0.136	9.54
XIII	$\left\{ \frac{1}{4}\text{H}_2 + \frac{3}{4}\text{CO} + \text{O}_2 + 4\text{N}_2 \dots \right\}$	21.95	3.55	14.20	60.30	20	50	409	8.2	0.025	0.158	9.12
XIV		22.90	3.60	14.30	59.20	20	50	418	8.36			
XV	$\left\{ \frac{1}{4}\text{H}_2 + \frac{1}{8}\text{CO} + \text{O}_2 + 4\text{N}_2 \right\}$	24.60	2.20	14.00	59.20	13	50	427	8.54	0.025 to 0.030	0.165	9.60
XVI		24.80	2.00	13.80	59.40	14	50	425	8.50			
XVII	$\left\{ \frac{1}{3}\text{H}_2 + \frac{2}{3}\text{CO} + \text{O}_2 + 4\text{N}_2 \right\}$	25.60	1.45	14.05	58.90	14.5	50	417	8.34	0.030	0.173	9.69
XVIII		25.50	1.10	14.30	59.10	13	50	425	8.50			
VIII	$200 + \text{O}_2 + 4\text{N}_2$ .....	28.6	Nil	16.0	55.4	18.2	50	421	8.40	0.180	—	10.23



but  $m+n=1$ ) are exploded at the same initial pressure. On the other hand, if their effects are not additive, then the cause of the disparity in question must be sought for elsewhere.

All that was needed to settle experimentally this fundamental issue was to explode a series of such isothermic mixtures at the same initial pressure (50 atmospheres), and, from the pressure records, to compare the time actually taken in each case for the attainment of maximum pressure with that calculated on the supposition that the separate influences of hydrogen and of carbon monoxide are additive. This was accordingly done in the series of experiments in Table IV, with results which were certainly conclusive against any such supposition.

The very decisive character of these results will be made clear by a comparison of the pressure curves (figs. 5, 6, and 7) obtained in Experiments X, XIV, and XVIII, respectively, with those already reproduced (figs. 1 and 4, respectively) in connection with the  $H_2$ -air and CO-air series, respectively.

It will be observed that in each of the above curves the sharp and almost vertical rise up to the point of maximum pressure, and the abrupt turning downwards thereafter, closely resemble the hydrogen-air curve (fig. 1, *q.v.*). Indeed, there was hardly any feature in the rising-pressure curves to suggest the influence of carbon-monoxide, except perhaps in the case of mixtures

Table V.—Analyses of the Pressure Curves in 3rd Series.

Experiment .....	II.	X.	XII.	XIV.	XVI.	XVIII.	VIII.
Ratio $H_2$ : CO in the mixture exploded	2 : 0	1 : 1	1 : 3	1 : 7	1 : 11	1 : 23	0 : 2
$t$ . (secs. after ignition).	P. atmos.	P. atmos.	P. atmos.	P. atmos.	P. atmos.	P. atmos.	P. atmos.
0·000	50	50	50	50	50	50	50
0·005	391*	—	175	—	—	—	—
0·010	—	350	350	65	63	—	—
0·015	385	399*	410*	—	—	—	—
0·020	—	—	—	—	108	—	—
0·025	380	395	405	418*	—	—	55
0·030	—	—	—	—	425*	425*	—
0·050	368	382	397	399	415	418	75
0·100	340	362	380	381	398	403	175
0·200	298	327	354	357	379	382	421*
0·300	264	302	333	341	363	365	412
0·400	242	278	318	327	349	352	395
0·600	198	243	291	307	327	332	373
0·800	174	219	270	289	309	312	352
1·000	152	194	248	273	292	298	332

The asterisk denotes the attainment of the maximum pressure ( $P_m$ ) in each case.



containing more than seven volumes of CO to one of  $H_2$ , where it could just be traced for something like 0.005 second after ignition, during which the initial part of the rising curve was a little rounded. All this means that, in some way or other which has yet to be explained, the presence of even 1 per cent. (and probably less) of hydrogen in a CO-air mixture, at the high initial pressures employed by us, has an altogether disproportionately large influence in accelerating the rise of pressure on explosion. Indeed, such a small proportion of hydrogen seems capable of imposing its own character upon the whole course of the subsequent combustion at such pressures.

Analyses of the cooling curves obtained in this series (*vide* Table V) are of some interest, in that they show very distinctly how the progressive replacement of steam by carbon dioxide in the products retarded the pressure-fall after the maximum point had been passed.

#### *Discussion of Results.*

(1) To chemists who have specially studied gaseous combustion, there has always been something peculiarly enigmatical about the very different behaviour, in many respects, of the two simplest combustible gases, carbon monoxide and hydrogen. And even those who have not gone very deeply into the matter must have been struck with certain obvious differences between their flames.

This enigma may perhaps best be expressed by saying that, whilst the volumetric heats of combustion of the two gases, and also the volumetric proportion in which each of them combines with oxygen, are the same:—

$$\begin{array}{l} \text{e.g., we usually} \left\{ \begin{array}{l} 2H_2 + O_2 = 2H_2O \dots 68.4 \\ 2CO + O_2 = 2CO_2 \dots 68.0 \end{array} \right\} \text{K.C.U. per gramme} \\ \text{write} \qquad \qquad \qquad \left\{ \begin{array}{l} 2H_2 + O_2 = 2H_2O \dots 68.4 \\ 2CO + O_2 = 2CO_2 \dots 68.0 \end{array} \right\} \text{molecule,} \end{array}$$

yet in almost all other respects their modes of combustion present a strikingly wide contrast.

(2) Thus, for example, (a) hydrogen-air mixtures have lower ignition temperatures, and, under similar physical conditions, propagate flame much faster than the corresponding CO-air mixtures; (b) the flame of hydrogen burning in air is smaller and "sharper" than a similar flame of carbon monoxide (*i.e.*, burning at the same orifice and under the same pressure); indeed, the CO-flame is always described as being "lambent," and its appearance suggests a *slower burning* gas than hydrogen; and (c) when corresponding  $H_2$ -air and CO-air mixtures are respectively exploded in a closed vessel, the pressure rises to a maximum *rapidly* in the case of hydrogen, but *slowly* in the case of carbon monoxide.

(3) These three contrasts all suggest that carbon monoxide has greater difficulty than hydrogen in getting oxidised in flames. In fact, ever since

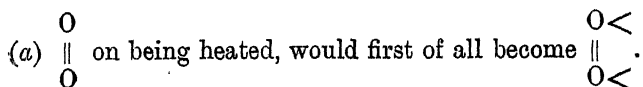
H. B. Dixon's classical researches, it has been known that the presence of even a minute quantity of steam greatly assists, if it is not absolutely essential to, the oxidation of carbon monoxide in flames. And it can easily be shown that a flame of the *dry* gas is extinguished on being introduced into a jar of air that has been dried over strong sulphuric acid. The precise mode in which steam accelerates or determines the combustion of carbon monoxide has, up to the present, never been completely explained; but chemists are generally agreed that the phenomenon in question is due to some peculiar inertness of CO for O<sub>2</sub> molecules in flames, which the presence of steam, somehow or other, overcomes. We are, therefore, justified in concluding that, in ordinary flames, carbon monoxide cannot interact with undissociated O<sub>2</sub> molecules.

(4) Another very significant difference between the respective behaviours of hydrogen and carbon monoxide in flames, which has already been referred to in the introductory portion of our paper, is the fact (first published by one of us in 1916) that, whilst what may be termed the "mass influence" of hydrogen upon the actual distribution of oxygen between the combustible constituents of a burning mixture is proportional to the *square* of its concentration, that of carbon monoxide is nearly proportional to the *first power* of its concentration. This can hardly mean otherwise than that, whereas the primary oxidation of hydrogen in flames involves the simultaneous action of two H<sub>2</sub> molecules, the primary oxidation of carbon monoxide does not require the action of more than one CO molecule.

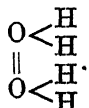
(5) Finally, in view of what has been brought to light during our present investigation, there must now be added to the other puzzling features of the problem the peculiar influence of hydrogen in accelerating the rise of pressure in the explosion of (H<sub>2</sub>+CO)-air mixtures at high pressures, an effect which has been shown to be altogether disproportionate to the volumetric amount of it present.

(6) Although a complete explanation of the foregoing facts is hardly yet possible, in the present state of our knowledge, we venture to put forward the following view tentatively, as worthy of consideration, in the hope that it may provoke and stimulate further discussion and research. It involves the conception that, whereas in certain cases of combustion (such as that of hydrogen), undissociated O<sub>2</sub> molecules can, and ordinarily do, interact directly with those of the combustible gas, yet in other cases (such as that of carbon monoxide), the dissociation of the O<sub>2</sub> molecules is a necessary precedent to the actual oxidation; or, in other words, that oxygen in flames may function in two distinct ways, namely (a), as undissociated O<sub>2</sub>, and (b) as dissociated and atomic O.

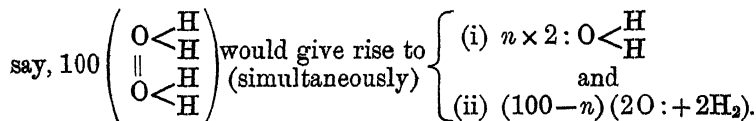
(7) According, then, to this conception, it may be supposed that an undissociated  $O_2$ -molecule, on being raised to a certain moderately high temperature in the flame, has its "residual affinities" sufficiently stimulated to enable it to seize upon, and grip hold of, two undissociated hydrogen molecules, forming initially an unstable vibratory complex  $H_4O_2$ , thus:—



(b) which, seizing upon two  $H_2$  molecules, would momentarily form the unstable complex,

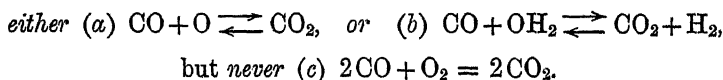


(8) Such a complex, being in an intensely vibratory condition, would instantly break down, partly (i) into two molecules of steam, also in a vibratory condition, and therefore chemically "activated," and partly also (ii) into two  $H_2$ -molecules and two O atoms, thus:—



The ratio  $(n/100-n)$  would obviously depend upon both temperature and environment; the higher the temperature, and the less hydrogen in the environment, the less the magnitude of  $n$ . In some such way, however, it may be supposed that hydrogen, in a combustible mixture containing also CO, could function as a resolver of  $O_2$  molecules simultaneously into (i) "activated" steam and (ii) O atoms.

(9) It is also further supposed that  $O_2$  and CO molecules are mutually inert in flames, and that, before the latter can be oxidised, the  $O_2$  must be resolved either into atoms or "activated" steam; thus, we might have:—



(10) Such a view would account for (a) the comparative slowness of the combustion of carbon monoxide, as illustrated by the slow rise in the pressure curve for the CO-air mixtures in our experiments; (b) the observed accelerating influence of both steam and hydrogen thereon; and (c) the fact that the "mass influence" of carbon monoxide upon the actual distribution of oxygen between the combustible constituents of a burning mixture is

proportional to the *first* power (and not, like that of hydrogen, to the *square*) of its concentration.

(11) The remarkable influence of hydrogen upon the rate of combustion of carbon monoxide in our experiments calls to mind the similar influence of steam first discovered by H. B. Dixon in the year 1880. In his later experiments upon the rates of detonation of  $(2\text{CO}_2 + \text{O}_2)$  mixtures containing varying proportions of steam, Dixon found that, starting with a well-dried mixture (fired at a pressure of 760 mm.), the rate increased, with successive additions of moisture, from 1264 to a maximum of 1738 metres per second for a mixture saturated with moisture at  $35^\circ \text{C.}$ , and therefore containing about 5.5 per cent. of steam.\* He also found that, on sparking a well-dried mixture of carbon monoxide (60 per cent.), chlorine peroxide (29 per cent.), and oxygen (11 per cent.), though a flame was propagated through the gases, as much as 76 per cent. of the original carbon monoxide may remain unburnt,† showing that, whilst dry “nascent” oxygen may be reactive towards carbon monoxide, some other condition (*e.g.*, its continuous reproduction at a high enough temperature) is needed to make it fully effective. Our experiments seem to point to hydrogen being even more potent than its equivalent of steam as a promoter of the combustion of carbon monoxide (though this is a matter needing further investigation), and they suggest that its primary function is to resolve continuously the inert  $\text{O}_2$  molecule into an “active” oxidising condition (*i.e.*, into O atoms and “activated”  $\text{OH}_2$ ), itself being continuously regenerated in some such manner as we have described.

(12) In addition to their bearing upon the theory of gaseous combustion, our results are of practical interest in connection with a question which has recently been much under discussion. In certain quarters it has become fashionable to assume that the relative values of different combustible gases are strictly proportional to their heats of combustion, irrespective of their chemical characters or modes of combustion. Such an assumption was, indeed, “tentatively accepted” by the Fuel Research Board in their “Report on Gas Standards” in 1919, although its endorsement was qualified by the admission that “experimental proof” of it “is still incomplete.”‡ It seems difficult to reconcile it with the cumulative results of the last forty years of scientific research upon gaseous combustion, which have shown more and more clearly that the fundamental properties of the explosive mixtures formed by different combustible gases with air, arising from their own peculiar chemical characters

\* H. B. Dixon, ‘Phil. Trans.,’ A, vol. 184, p. 187 (1893).

† H. B. Dixon and E. J. Russell, ‘Trans. Chem. Soc.,’ vol. 71, p. 605 (1897).

‡ Cmd. 108, p. 5.

and compositions, do affect profoundly their economic uses. The results of the present research emphasise the importance of the chemical composition of a combustible gas (or mixture) as a factor which cannot be disregarded when its economic value is in question.

Further experiments at high pressures are in contemplation to develop the matters dealt with in this paper; and it is intended also to make similar experiments at atmospheric pressure.

Our thanks are due (*a*) to the Government Grant Committee of the Society for grants out of which the cost of the expensive apparatus employed in the research has been defrayed, and (*b*) to the Salters' Institute of Industrial Chemistry for the Fellowship granted to one of us (W. A. H.) to enable him to devote his whole time to the work.

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### *On the Spectra of Lead Isotopes.*

By T. R. MERTON, F.R.S.

(Received July 12, 1921.)

In a previous communication\* an account was given of comparative measurements of the wave-length of the line  $\lambda = 4058 \text{ \AA}$ . in the spectra of ordinary lead and of the leads obtained from uranium and thorium minerals respectively. The line  $\lambda = 4058 \text{ \AA}$ . is the strongest line in the arc spectrum of lead and the results obtained were

$$\lambda (\text{lead from pitchblende}) - \lambda (\text{ordinary lead}) = 0.0050 \pm 0.0007 \text{ \AA}.$$

$$\lambda (\text{ordinary lead}) - \lambda (\text{lead from thorite}) = 0.0022 \pm 0.0008 \text{ \AA}.$$

The lead from pitchblende had been extracted from some Joachimstal pitchblende residues, and since this mineral is known to be free from thorium there was no reason to suspect that the sample of lead obtained was contaminated with lead of a thorium parentage. It was not known whether any ordinary lead was present but the wave-length difference which was found agreed closely with the value found by Aronberg\* in a comparison of the same spectrum line of ordinary lead and a sample of lead from Australian Carnotite for which Prof. Richards had found an atomic weight of 206.318.

\* 'Roy. Soc. Proc.,' A, vol. 96, p. 388 (1920).

† 'Astrophys. Journ.,' vol. 27, p. 96 (1918).

The thorium lead had been given to me through the kindness of Prof. Soddy and had been extracted from the mineral thorite, and it was known to be not entirely free from contamination by lead of a uranium parentage, since thorite contains a small proportion of this element.

It is a matter of some interest to discover whether this wave-length difference, or the corresponding wave-number difference, is to be found between all corresponding lines in the spectra of the isotopes; whether the spectrum lines are shifted as a whole or whether different lines are affected to a different extent or in a different direction. Very little remained of the samples which had been used in the previous investigation, but I have recently received, through the kindness of Mr. Lambert, a relatively large quantity of a sample of lead from Australian Carnotite, and it was accordingly decided to compare a number of lines in the spectrum of this sample with the lines in ordinary lead.

The method of measurement and reduction has been described fully in the previous investigation (*loc. cit.*). In the present measurements a Hilger quartz spectrograph was used to separate the fringe systems produced by the étalon in place of the glass spectrograph which was used previously, owing to the absorption of the more refrangible radiations by the glass prism. It has been pointed out (*loc. cit.*) that certain experimental errors can be avoided by using as a source an electric arc burning *in vacuo* with a pole consisting of an alloy of the sample of lead under investigation and cadmium, the wave-lengths being thus determined on each plate in terms of a selected cadmium line, but it has been found that the plates which were most suitable for the comparison of the lead line  $\lambda = 4058 \text{ \AA.}$  with the cadmium line  $\lambda = 4800 \text{ \AA.}$  were not so well adapted for the comparison of the more refrangible lead lines, and it has therefore been found more convenient to carry out the measurements in two parts, that is to say a comparison of the line  $\lambda = 4058 \text{ \AA.}$  from the Carnotite lead and from ordinary lead with a cadmium line, and a comparison of the different lines with one another in each sample of lead.

The only objection to this procedure appears to be that in so far as the absolute values of the differences in the two spectra are concerned the probable error in the difference found for  $\lambda = 4058 \text{ \AA.}$  must be added to the probable errors for each of the more refrangible lines, but this consideration does not apply to the relative shifts found for the different lines. It may be recalled that since the differences in wave-length are small it is only necessary to determine the fractional values ( $f$ ) of the orders at the centres of the ring systems and to reduce these to the same standard of  $f=0$  for the standard line. Two series of three plates each for each sample of lead, gave the following results, the cadmium line  $\lambda = 4800 \text{ \AA.}$  being used as

standard. The difference in wave-length corresponding to a shift of a whole order is equal to  $\lambda^2/2d$ , where  $\lambda$  is the wave-length of the line and  $d$  the thickness of the étalon, which in these experiments was 9.80 mm.

Values of  $f$  (reduced to  $f = 0$  for cadmium  $\lambda = 4800 \text{ \AA}$ ).

Ordinary lead.	Lead from Carnotite.
0.293	0.171
0.292	0.158
0.294	0.180
0.277	0.191
0.275	0.158
0.294	0.160
Mean = $0.287 \pm 0.004$	$0.170 \pm 0.006$

$$\text{Difference} = 0.117 \pm 0.010.$$

$$\lambda (\text{lead from Carnotite}) - \lambda (\text{ordinary lead}) = 0.0098 \pm 0.00084 \text{ \AA}.$$

A further set of three pairs was taken on plates on which the cadmium standard  $\lambda = 4800 \text{ \AA}$ . was not recorded and in reducing these plates the cadmium line  $\lambda = 3404 \text{ \AA}$ . was used as a standard, though the fringes obtained with this line were not quite so well defined as in the case of  $\lambda = 4800 \text{ \AA}$ . The results were as follows:—

Values of  $f$  (reduced to  $f = 0$  for cadmium  $\lambda = 3404 \text{ \AA}$ ).

Ordinary lead.	Lead from Carnotite.
0.725	0.557
0.700	0.559
0.692	0.563
Mean = $0.706 \pm 0.010$	$0.560 \pm 0.002$

$$\text{Difference} = 0.146 \pm 0.012.$$

$$\lambda (\text{lead from Carnotite}) - \lambda (\text{ordinary lead}) = 0.012 \pm 0.001 \text{ \AA}.$$

From these results it is believed that a value for the difference in wave-length of  $0.011 \pm 0.0008 \text{ \AA}$ . may be adopted. This value is of the same sign but rather more than twice as great as that obtained in the previous investigation in which ordinary lead and lead from pitchblende residues were compared. The most probable explanation of this difference is evidently that the Carnotite lead used is a purer sample of uranium lead than that obtained from the pitchblende residues. There remained the very remote possibility of some difference between the "ordinary" leads used, a sample

from Kahlbaum having been used in the former measurements, whilst a sample of assay lead from Messrs. Johnson and Matthey was used in the experiments recorded above. As a sample of the Kahlbaum lead was still available, three pairs of plates were taken to compare the wave-length of the line  $\lambda = 4058 \text{ \AA.}$  in these two samples, but the discrepancy between the values obtained amounted to only one thousandth of an Ångström: a difference which is too small to be considered as having any real significance.

A number of attempts have been made to observe the line  $\lambda = 4058 \text{ \AA.}$  as a close double in the spectrum of an alloy of the two leads, using a 35 plate échelon with plates 15 mm. thick. The observation should be just within the resolving power of the instrument, but it was not possible to obtain any positive results owing to the widths of the lines. Four other lines  $\lambda\lambda = 3740, 3684, 3640$ , and  $3573 \text{ \AA.}$  have been compared with  $\lambda = 4058 \text{ \AA.}$  in the spectra of the Carnotite and ordinary lead, these being the only lines which were bright enough for investigation with the apparatus at present available. Three pairs of plates have been measured; the details are not given, being similar to those given above for the line  $\lambda = 4058 \text{ \AA.}$ , but the final results are set forth in the following table:—

$\lambda$	$\lambda$ (Carnotite lead) — $\lambda$ (ordinary lead).	Wave-number (ordinary lead) — Wave-number (Carnotite lead).
4058	$0.011 \pm 0.0008 \text{ \AA.}$	$0.065 \pm 0.005$
3740	$0.0074 \pm 0.0011 \text{ \AA.}$	$0.053 \pm 0.008$
3684	$0.0048 \pm 0.0007 \text{ \AA.}$	$0.035 \pm 0.005$
3640	$0.0070 \pm 0.0003 \text{ \AA.}$	$0.052 \pm 0.002$
3573	$0.0048 \pm 0.0005 \text{ \AA.}$	$0.037 \pm 0.004$

It has already been pointed out that in so far as absolute values of the differences are concerned, the error for  $\lambda = 4058 \text{ \AA.}$  should be added to those for the other lines. It is apparent that the differences are not the same for the different lines though they appear to be almost identical for the lines  $\lambda\lambda 3740 \text{ \AA.}$  and  $3640 \text{ \AA.}$ , and for  $\lambda\lambda 3684 \text{ \AA.}$  and  $3573 \text{ \AA.}$  This result is somewhat surprising, for although little is known of the series relations in the spectrum of lead, the lines  $\lambda\lambda 3740 \text{ \AA.}$  and  $3573 \text{ \AA.}$  are members of a group which is related to other groups in the spectrum by constant differences in wave-number, and a similar behaviour might therefore have been expected in these lines; but the apparent agreement in the displacements of the two pairs of lines may be partly accidental. The difference in the line  $\lambda = 4058 \text{ \AA.}$  in the two isotopes is about two hundred times as great as would be expected on Bohr's theory, if the difference is calculated in the same manner as the difference between the Balmer lines of hydrogen and the



enhanced helium lines; but as the theory has not yet been extended successfully to the arc lines of the heavier elements, the comparison is of no great value.

I should like to express my indebtedness to Mr. S. Barratt for his help in making the measurements, and to Mr. Fensom for his skilful assistance.

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*The Adsorption of Gas by Charcoal, Silica, and other Substances.*

By HENRY BRIGGS, D.Sc., Ph.D., Professor of Mining, Heriot-Watt College, Edinburgh.

(Communicated by Prof. J. F. Thorpe, F.R.S. Received March 9, 1921.)

1. *Introduction.*

The experimental work here described was carried out on behalf of the Oxygen Research Committee and the Mine Rescue Apparatus Research Committee of the Scientific and Industrial Research Department. The main object of the experiments was to investigate the possibility of obtaining a non-inflammable substitute for the activated charcoal used in metal vacuum flasks intended for holding liquid air. The work was eventually extended so as to include an examination into some of the more theoretical aspects of gas adsorption.

The special problems presented by the metal vacuum vessel made it necessary to pay particular attention to the adsorption of nitrogen at liquid air temperature. Many measurements have also been made using hydrogen.

2. *Preparation of Non-inflammable Adsorbents; their Capacity at Liquid Air Temperature.*

A large number of non-inflammable substances were prepared and were tested to ascertain their capacity for nitrogen at the temperature of boiling liquid air and at normal pressure. The liquid air used had an average composition of 50 per cent. oxygen and 50 per cent. nitrogen; this mixture boils at  $-190^{\circ}\text{C}$ . The materials, which were in the granular state, were tested in a uniform manner. Immediately before being used, each sample was heated in a gas-oven for several hours at a temperature of  $300^{\circ}\text{C}$ . The sample was inserted, while hot, into a hot brass retort, holding 25 c.c., and well shaken down. A cap, having a copper tube brazed into it, was screwed

to the retort and a pressure test was applied to try the joint; the tube was then connected to a large gas-burette, containing nitrogen standing over strong sulphuric acid. The retort being placed in a bath of cold water, which furnished a definite initial temperature, the burette was read. The retort was then immersed in liquid air and allowed to stay there until no more gas was drawn in. After the state of saturation had been reached, the retort was withdrawn from the liquid air and allowed to regain its original temperature; the volume of gas expelled was measured as a check on the volume absorbed during cooling. A blank experiment made with an empty thimble gave the correction to be applied for contraction of the gas in the thimble and connecting pipe and for condensation upon the metal surfaces.

Of the mineral substances tried meerschaum proved the best, though its capacity at  $-190^{\circ}$  C. was greatly inferior to that of the better kinds of charcoal and silica. Preparations of colloidal alumina and stannic acid were also tried, but were found of little value.

In the following Table, the gas volumes are expressed at N.T.P., and they relate to the amount adsorbed between  $18^{\circ}$  C. and  $-190^{\circ}$  C. "Gross volume" includes the interstitial spaces, or voids, between the granules.

Table I.—Adsorption of Nitrogen and Hydrogen at Liquid Air Temperature and Atmospheric Pressure.

No.	Substance.	Dry nitrogen.		Dry hydrogen.		<u>Hydrogen</u> <u>Nitrogen</u>
		C.cs. ad- sorbed per c.c. (gross vol.) of sub- stance.	C.cs. ad- sorbed per grm. of sub- stance.	C.cs. ad- sorbed per c.c. (gross vol.) of sub- stance.	C.cs. ad- sorbed per grm. of sub- stance.	
1	Cocoonut charcoal (activated by steaming)	129	247	66.3	127	0.60
2	Plumstone charcoal (activated)	91.2	—	56.7	—	0.72
3	Birch charcoal (activated).....	44.5	202	27.0	123	0.62
4	German impregnated charcoal (1918)	121	303	25.5	63.8	0.28
5	Blood charcoal .....	91.1	—	36.3	—	0.40
6	Sutcliffe-Speakman's prepara- tion of briquetted coal and charcoal dusts	91.8	206	43.1	96.7	0.47
7	Cleveland (U.S.A.) activated anthracite	84.9	89.7	53.1	56.3	0.63
8	Graphite, ground .....	5.6	—	2.7	—	0.49
9	Colloidal silica.....	203	376	26.7	51.6	0.13
10	Dried silica gel (Baltimore, U.S.A.)	115	142	—	—	—

A silica (No. 9) can now be made whose capacity for nitrogen, at  $-190^{\circ}\text{C}$ . and atmospheric pressure, is, on the volumetric basis, greater than that of the best charcoal by 66 per cent. The secret of preparation of a high-capacity silica mainly lies in the temperature of drying and in the thorough cleansing of the substance of common salt. The optimum temperature was found to be  $300^{\circ}\text{C}$ . Many ways of de-watering and washing the gel were tried, the most satisfactory being the following:—The unwashed gel (made from water glass) was dried at  $300^{\circ}\text{C}$ . in a gas-oven and plunged while hot into hot distilled water. Washing by decantation was continued until the wash-water was free of chloride; the substance was then dried in the oven for a second time, and was again plunged into hot water, the cycle of operations being continued until the material, when dropped into water, yielded no trace of chloride. As a final test, some of the silica was boiled with weak silver nitrate solution, to make sure that there was no opalescence. This treatment gave better results than dialysis. Drying in the gas-furnace at a steady temperature of  $300^{\circ}\text{C}$ . proved preferable to drying by electric endosmosis. A large number of preparations were made in which the silica was mixed at the sol stage with organic sols such as agar and Irish moss, in order to produce a carbonaceous silica, but the adsorptive capacity was not improved thereby. It was found that carbon in small amount could be introduced by heating the silica and placing it in thick smoke, but again the treatment gave no advantage. The addition of an iron salt to the silica sol proved to be deleterious. Heating the pure silica to  $900^{\circ}\text{C}$ . for a short time, to dispel the last portion of its combined moisture, also resulted in a decrease of capacity.

### 3. *Preferential Adsorption.*

The phenomenon of preferential gas adsorption is revealed most clearly when the properties of two or more adsorbents are compared. Thus the striking partiality of charcoal and carbonaceous adsorbents for hydrogen stands out in high relief when those substances are contrasted with silica, as is to be seen by the last column of Table I, in which is given the ratio between the hydrogen and nitrogen adsorbed.

In discussing a recent paper by N. K. Chaney (1), H. H. Sheldon stated that he had succeeded in making a charcoal which, at liquid air temperature, was more active upon hydrogen than upon nitrogen; the three examples he quoted give H/N ratios of 1.3, 1.2 and 2.1 respectively.

It seems necessary to assume the existence of a high specific attraction between the molecules of the two elements, carbon and hydrogen. That the preference does not result from the state of porosity of the adsorbent is indicated by the fact that the non-porous graphite (No. 8) was found to have

at  $-190^{\circ}\text{C.}$ , a H/N ratio much the same as that of the very porous blood charcoal (No. 5).

#### 4. *Determination of Density and of the Solid and Gaseous Volumes of Charcoal and Silica.*

In a sample of granulated charcoal or silica the gross volume is made up of:—

(a) The volume of the solid.

(b) The interstitial volume, *i.e.*, that of the open spaces, or voids, between the granules.

(c) The volume of the capillaries and polymeral interstices existing within the granule; this being spoken of below as the *internal gaseous volume*.

It was important to ascertain the relation between these volumes, and especially between (a) and (c).

Mitscherlich (3), employing the immersion method, found the charcoals used by him to consist, in the piece, of about 39 per cent. of solid matter and 61 per cent. of internal gaseous volume. W. D. Harkins and D. T. Ewing (3) ascertained the "pore" volume to range between 53.4 per cent. when water, and 59.3 per cent. when pentane was the liquid used. E. B. Miller (4) and his associates estimated that in dried silica gel (No. 10, Table I) the internal gaseous volume was 41 per cent. of that of a granule.

In obtaining the solid volume, I placed the sample, whether of charcoal or of silica, in a dry graduated tube; shook it well down, and observed its gross volume. Its weight *in vacuo* was next found. The sample was then heated and thoroughly evacuated by being connected, through a three-way tap, to a much larger bulb holding dry cocoanut charcoal and immersed in liquid air. After cooling the sample, the tap was turned and air-free water was allowed to enter the exhausted tube to a definite mark. The routine then followed that of the ordinary specific gravity bottle method. As has been shown by Harking and Ewing (3) and by A. M. Williams (5), the specific gravity and, therefore, the proportional volume of the solid determined in this way is affected by error, due to the high density of the layer of liquid actually in contact with the solid. It is clear that, under the agency of the error in question, a specific gravity so computed will be too high; that the more active the adsorbent the more serious will be the error involved, and also that the error will increase with the compressibility of the liquid employed. Williams has discussed (5) the possible incidence of another factor militating against the accuracy of the results obtained by the immersion method, namely that of inadequate penetration, especially by large molecules such as those of chloroform, into the more minute intermolecular openings of the solid. An

error of this character, however, would operate in the opposite sense to that due to compressibility and would tend to reduce the latter; further, when water is the liquid used it is difficult to imagine that there can be, in any part of a charcoal, an opening so small that the water molecule cannot enter, looking to the fact that these channels have been the vents through which larger hydrocarbon molecules made their escape during the carbonising process. In silica, again, where water was the only compound driven off in the gaseous condition during treatment, the passages through the solid must have served in the first place for the egress of steam, and, therefore, they are presumably accessible to the water molecule, though not necessarily to larger molecules.

Harkins and Ewing (3) found that the density of a certain activated cocoanut charcoal, as ascertained by immersion, varied between 1.843 when water was used, to 2.129 when pentane was employed. Other densities of cocoanut charcoal (ascertained by water-immersion) quoted by these workers are: 1.863, 1.835, 1.808; Titoff (6) gave 1.86, Baerwald (7) 1.92 and Miss Homfray 1.66. Hulett (quoted by Chaney (1)) got the value 1.84. I found the density of activated cocoanut charcoal (No. 1, Table I) to be 1.88, and that of "raw" cocoanut charcoal to be 1.74. For the reasons given, the former value is certainly higher than the true density.

Williams (5) found the specific volume of blood charcoal, by immersion in chloroform at 25° C., to be 0.46; by an able theoretical analysis based upon the experimental facts he then shows that, owing to compression of the chloroform, this value was too low by 0.21. That is to say, the true specific volume of the blood charcoal he used was 0.67 c.c. per gramme, and the equivalent density was 1.49. He had previously determined the density by water-immersion to be 1.96—a figure which therefore turned out to be 32 per cent. higher than the true value.

The intensity of the forces of attraction at the surfaces of such a silica as No. 9, Table I, though greatly less than in the case of charcoal, is appreciable, and, in consequence, the specific gravity of the silica ascertained by the immersion method is also apt to be too high. As will subsequently appear, it is possible with silica to de-activate it completely; hence the apparent density in the inactive and active states may easily be compared. The water-immersion method gave 2.30 as the specific gravity of No. 9 and 2.00 as that ratio after de-activation. The difference would doubtless have been greater but for the fact that, during de-activation, the silica lost combined water.

In the case of cocoanut charcoal the most satisfactory way of measuring the proportion of *interstitial space* between the granules was to place a sample, well shaken down, in a wide tube of known volume, the inlet and outlet to

the tube being by capillary stems into which the granules were too large to enter, and then to fill the interstices by admitting mercury. As the mercury did not wet the charcoal, the adsorbed gas remained quiescent. The volume of mercury entering between the granules was found by weighing.

With only one of these substances was it found possible to get a reliable direct measurement of internal gaseous volume, namely with the de-activated variety of silica to which allusion has already been made. This was done by means of a glass apparatus which enabled a sample of silica to be evacuated under water; after exhaustion normal pressure was restored, the gas emitted by the silica was discharged from the apparatus, and the volume of water entering the "pores" was measured on a capillary stem. The measurement was reasonably reliable because de-activated silica has zero retentivity; therefore it parted with its gas readily under the influence of the relatively imperfect vacuum applied, and the water did not pass under compression when it entered the internal spaces vacated by the air.

De-activated silica was found in this way to have an internal gaseous volume amounting to 6 per cent. of the gross volume.

The figures of the following Table do not take into account the compressibility of water and must merely be regarded as providing a first estimate, which will need revision at a later stage. Obviously, with the two active substances, the whole of the error affecting the evaluation of the solid volume affects that of the internal gaseous volume, and as the former is too low the latter must be too high.

Table II.—Estimates of the Proportional Volume of Solid Matter, Internal Spaces and of Voids, uncorrected for Effect of Compressibility of Water.

Substance.	Volume of solid matter.	Internal gaseous volume.	Interstitial space.
	per cent.	per cent.	per cent.
Activated cocoanut charcoal (No. 1, Table I)	28	32	40
Activated colloidal silica (No. 9, Table I) ...	27	30	43
De-activated silica .....	51	6	43

According to these values, the internal gaseous volume constitutes 53 per cent. of the volume of a granule of the charcoal; the equivalent proportions for granules of active and de-activated silica are 53 and 10½ per cent. respectively.

5. *State of Adsorbed Gas; Further Consideration of the Density of the Solid Matter.*

The volume of dry nitrogen taken in at atmospheric pressure and 18° C. was determined for dry cocoanut charcoal (No. 1, Table I) and dry silica (No. 9). The sample was placed while hot in the brass retort, well shaken down; the cap (with copper tube attached) screwed tightly into place, and the joint tested for leakage. The tube was connected to a burette containing nitrogen, standing over strong sulphuric acid. The retort having been placed in a water bath at 18° C., the burette was read. The retort was then put in a small electric pot furnace, the temperature was slowly raised above 300° C., and the volume expelled measured. The retort was then cooled and the volume drawn in again observed. By alternately heating and cooling several times in this manner a reliable mean value was obtained. The mean was corrected by subtracting the volumetric difference due to simple expansion or contraction between the temperature extremes, which was ascertained from a blank experiment. The results are given on the first line of Table III; the second line is copied from Table I.

Table III.—Adsorption of Dry Nitrogen at Atmospheric Pressure,  
per c.c. of Gross Volume.

	Cocoanut charcoal.	Silica.
Adsorbed at 18° C. ....	c.cs. (N.T.P.). 5·5	c.cs. (N.T.P.). 5·5
Adsorbed between 18° C. and -190° C. ....	129	203
Total adsorbed at -190° C. ....	134·5	204·6

Dewar (9), making use of Mitscherlich's value for the internal gaseous space (*vide sup.*), estimated the density of nitrogen adsorbed in charcoal at the boiling-point of the gas to be 1·00, a value approximating to the density of solid nitrogen, 1·026. We may now attempt a similar estimation by the aid of the figures of Tables II and III. Thus, in the case of silica, 204·6 c.cs. of nitrogen at N.T.P. (Table IV) weigh 0·256 gm., and if, as Table II may lead one to infer, this mass is condensed in a volume of 0·30 c.c., its *average* density, when adsorbed at -190° C., must be 0·83. A similar determination for the charcoal gives 0·53 as the density of the adsorbed nitrogen at the same temperature. The density of liquid nitrogen, according to Baly and Donnan (10), is 0·808 at -195° C. (its boiling-point at N.P.) and 0·785 at -190° C.

Judging from the stated result for silica, the density of the adsorbed gas

exceeds that of the liquid at the temperature in question, but it would appear that the reverse is true for charcoal. We know, however, that the specific attraction—*i.e.*, the force subsisting between the solid and the gas molecules—is much greater with charcoal than with silica, and on that account would expect the nitrogen to be held in a denser condition in the charcoal. We also know from Dewar's experiments on the heat of adsorption (11), and from the observations and calculations of Williams (5) and others, that, in the stated circumstances, the gas must exist in charcoal in a state which is denser than the liquid. Clearly, then, the above estimate (0.53) of the specific gravity of the nitrogen adsorbed in charcoal is too low. The error is due to the fact that when Table II was drawn up, no account was taken of the compressibility of the water used in determining the density of the charcoal. In consequence (see Section 4), the estimate of internal gaseous volume was too high; hence the computed specific gravity of the adsorbed gas is too low. For the same reason, the value (0.83) for the density of the nitrogen adsorbed by silica will also be too low, though the error will, in this case, not be so large.

If 0.83 be assumed to be the correct value in the instance of cocoanut charcoal (and the evidence, as we have just seen, points to this being a low estimate), the internal gaseous volume amounts to only 20.4 per cent. of the gross volume of the granules; the volume of the solid matter amounts to 39.6 per cent. and the true density of the charcoal works out at 1.33. It may therefore be safely inferred that the true density of the cocoanut charcoal I used was under 1.33, instead of being 1.88, as appeared from the water-immersion determination.

So far attention has been principally focussed upon the case in which an adsorbent has been allowed to saturate itself at normal pressure and at a temperature only a few degrees above the boiling-point of the gas adsorbed. Let us now consider the other extreme, namely, the adsorption of a gas at low pressure or low partial pressure. In these circumstances the action differs markedly from that at high concentrations in that it follows Henry's law (2, 12). The same holds true, very nearly, for the adsorption of gases like nitrogen, oxygen, or hydrogen at ordinary temperature and moderate pressures, and, as Miller's recent work shows (4), for  $\text{SO}_2$  adsorbed by silica at temperatures of  $100^\circ \text{C}$ . or more. At these low concentrations the attraction of the gas molecules for each other must be an influence altogether negligible in comparison with the attraction between the gas and the solid—a force which Williams (5) calculates to be such that it is able to cause an aggregation of adsorbed molecules upon the surface of activated charcoal equivalent to that resulting from a pressure of about 10,000 atmospheres.



Adsorption at low concentrations must depend, then, upon (*a*) the magnitude of this attraction (the specific attraction of the solid), and (*b*) the extent of solid surface exposed to the gas. It will not depend upon the internal gaseous volume, since that volume is no criterion of the exposed surface.

As the concentration is increased, the packing of the gas molecules upon the surfaces will also increase in density. Sooner or later a stage will be reached at which the gas molecules can only accumulate by adhering to others already anchored, and then the attraction of the molecules for each other will become a factor of importance. Eventually, as the temperature and pressure become such as to bring the outside gas near to liquefaction, the adsorption of gas molecules upon surfaces consisting of anchored gas molecules will proceed at an intensified rate; the finer, and finally the coarser, capillaries will fill up. The volume of gas (expressed at N.T.P.) which can be taken in at complete saturation will depend upon (*a*) the specific attraction of the solid as determining the firmness of anchorage of the initial layer and the degree of compression of that layer; (*b*) the thickness of the layer of compression; (*c*) the exposed surface as determining the extent of the layer of compression; (*d*) the compressibility of the liquefied gas; (*e*) the "internal gaseous volume" of the adsorbent, now filled with liquid; and (*f*) the relation between the densities of the gas and its liquid.

As the attachment of gas molecule to gas molecule at this latter stage cannot of itself produce a mass denser than the liquid at the particular temperature, and, as the average density of the adsorbed gas has, in these circumstances, been shown to be greater than that of the liquid, it follows that the attraction of the solid for the gas molecule is greater than the attraction of the gas molecules for each other. It seems likely that we have, in this latter relation, one of the conditions essential to adsorption.

The differences between the characteristics of adsorption at low and high concentrations make it impossible to judge of the former from the volume of gas taken in during complete saturation; hence the figures of Table I bear no relation to the retentivity of the substances. Because it has a high capacity for nitrogen at normal pressure and  $-190^{\circ}$  C., a substance is not necessarily suitable for producing high vacua.

When the state of complete saturation is at hand, each granule will be surrounded by a thin halo or envelope of condensed gas. The condensation effected by graphite, which has zero internal gaseous volume, must be entirely due to such an envelope, and, as Table I shows, this is by no means negligible with nitrogen  $5^{\circ}$  above the boiling point of the gas. The argument used earlier in this Section, to the effect that at complete

saturation the internal gaseous volume is altogether occupied by liquid, should, strictly speaking, be modified to the extent needed to take this envelope into account. The correction implied would slightly reduce the computed average density of the adsorbed gas, though not sufficiently to affect the conclusions drawn.

#### 6. *The Constitution of an Adsorbent.*

When we turn from a consideration of the gas adsorbed to an analysis of the characteristics of the solid substance, which acts both as condenser and as reservoir for that gas, we meet with phenomena, such as that of activation, whose effects can be studied by experiment, but whose intrinsic nature, to a great degree, yet remains in doubt.

It is unsatisfactory to speak of gas molecules being condensed upon the surface of the solid, since, if the gas is to be referred to the molar scale, so must the solid; such a statement, indeed, compels the question, The surface of what? In the present state of our knowledge of the constitution of solids, there appears to be no clear answer to that question; we are reasonably sure, however, that, in solid substances such as carbon and silica, we are not dealing with the ultimate molecule\* but with elaborate polymers.

Apparently, the only solid structures which are impervious to gas are the crystal and the glass. As is well known, the former can hold indefinitely gas "included" under pressure, while the latter, whether common glass, vitreous porcelain, or fused silica, can hold a high vacuum—and there is no better test of tightness—as long as the character of the glass remains unchanged. That these two forms possess so unusual a characteristic in common makes it probable that they have analogous structures; that, in fact, in place of being a molecular aggregate (which would be pervious to gas), a piece of glass, like a crystal, is a single atomic linkage, and as such is entirely free from interstices on the molar scale. If this view be allowed, it is clear that an adsorbent must be non-vitreous—an aspect of the question which is further considered below.

It has already been seen, in Section 3, that the chemical character of the material affects its properties as a gas-adsorbent. With any given material, there are two factors which have a profound influence on adsorptive power, namely, (a) the degree of canalisation of the substance, *i.e.*, its porosity on

\* I am indebted to Sir James Walker for suggesting the expression "ultimate molecule" to distinguish between  $H_2O$  and  $H_{2n}O_n$ , for example, or between the ultimate molecule  $SiO_2$  and the polymeride  $n(SiO_2)$ . The expression removes much of the ambiguity of meaning attaching to the word "molecule," which is not now always used in the original sense.

the microscopic or ultramicroscopic scale, and (b) the degree of porosity on the molar scale.

The microscopic or ultramicroscopic canals, whose presence as an intricate network of connected passages is so striking a feature of a high-capacity adsorbent, important though their function is, do not alone determine adsorptive power. A high-capacity silica may be de-activated by prolonged heating, and though, in the de-activated state, one-fifth of the original internal gaseous volume remains, the amount of gas it can take in is virtually *nil* even at liquid air temperature. Evidently the capillaries are only of use when they traverse a medium in a suitable physical condition. Again, powdered graphite, which has no capillary passages, is able to adsorb 5.6 times its gross volume of nitrogen at  $-190^{\circ}\text{C}$ .

The largest canals of charcoal can be seen under the microscope and Saussure, who measured the size of the cells of charred wood, found them to be, on the average,  $10^{-3}$  cm. in diameter, or about 13,000 times the diameter of a nitrogen or oxygen molecule. On the other hand, Lamb, Wilson and Chaney (13), from a study of the vapour-pressure curves of adsorbed liquids, estimated the average diameter of the pores (assumed to be cylindrical) of activated charcoal—including the finest with the coarsest openings—to be about  $5 \times 10^{-7}$  cm., which is less than seven times the diameter of the gas molecule. It may be inferred from these figures that the greater part of the internal gaseous space of an efficient adsorbent consists of passages which are not greatly larger than the gas molecule.

To draw an analogy: the coarser canals traversing the adsorbent may be compared with the bronchi of the lungs and the finer openings with the alveoli. Either kind of passage is useless without the other and their functions differ: the coarser canals convey and distribute the gas with a minimum of impediment, but (excepting in conditions approaching total saturation) they do not hold it; the gas is chiefly held on the surfaces of the polymers in openings of molar dimensions.

It will be evident that a higher degree of porosity on the molar scale and a greater exposure of surface will occur when the polymers are small rather than large; and that (other conditions remaining constant) if we can disrupt the elaborate polymers which build up a solid, the more active the material will become in adsorbing gas.

Reference has already been made to the fact that a high-capacity silica may be converted into a non-adsorptive substance by heating. The change is not due to the destruction of the capillaries, for 20 per cent. of the original porosity remains after heating. Had adsorption been merely a matter of pore-space, one-fifth of the original capacity—or, at  $-190^{\circ}\text{C}$ ., about forty

volumes of nitrogen per volume of silica—would have survived. Actually, the capacity fell almost to zero. The question arises: What happened to this silica to cause de-activation? The microscope showed the particles to be unchanged in outward form, but here and there in the mass there was evidence of incipient fusion, which was revealed by the occasional presence of a few of the finest particles enclosed by a skin. At first it was thought that the formation of surface skins might explain the loss of adsorptive power, but when a sample was finely ground there was no improvement: the change had affected the whole mass.

The evidence favours the explanation that the heating, without destroying the coarser passages, had vitrified the silica, and blotted out the finest openings upon which adsorption so largely depends. In other words, the heating had converted a granule which was originally an aggregate of small polymers riddled with openings into a completely polymerised unit impermeable on the molar scale.

#### 7. *Activation.*

It has long been known that if charcoal, and preferably a dense charcoal, be subjected to long-continued heating in the presence of a small amount of oxygen, its power of adsorption is greatly increased. This, the earliest process of activation, was developed by Dewar in connection with the charcoal used by him for obtaining high vacua; it has been discussed lately by Philip, Dunnill and Workman (14). Recently, it was discovered in this country that activation could be secured in a shorter time by the use of superheated steam, and this process, known as the steaming process, was considerably used towards the end of the war, both in America and Great Britain. Lamb, Wilson, and Chaney (13) state  $350^{\circ}$  to  $450^{\circ}$  to be the optimum temperature in the older, or air-activation process, though in this country it has been usual to carry it out at a considerably higher temperature. These writers advance the theory that activation mainly results from driving off the hydrocarbons which are residual in raw charcoal. No doubt the clearing of the charcoal of these substances is beneficial; but that it forms the chief object in activation is unlikely. The theory falls under three objections: First, the small amount of volatile hydrocarbon which is left to be driven off in this manner is disproportionate to the result produced. Secondly, though the presence of oxygen would help in breaking up the hydrocarbons, it would not be essential to their ejection; actually oxygen is found to be a necessity in the activation of charcoal (14). And thirdly, the residual hydrocarbons, as Chaney (1) has shown, require a temperature exceeding  $1000^{\circ}$  C. before they are all dispelled—a fact which

appears difficult to square with the theory if  $350^{\circ}$  to  $450^{\circ}$  is the optimum in air-activation. Chaney's later hypothesis (1), that active and inactive charcoal are different isotopes, does not seem to be sufficiently supported by evidence.

The most probable explanation of the activation of charcoal would appear to be that, in common with other highly polymerised substances, its structure is apt to be simplified by heat. Heating to  $1000^{\circ}$  C. without oxygen has no permanent effect. In other words, any cleavage or simplification of the polymers which may result from raising the temperature in a reducing atmosphere is followed by a re-union on cooling. But, if a little oxygen (either from air or from steam) be available when the polymers are split, some of the carbon is removed as  $\text{CO}_2$ ; their cleavage is perpetuated; the porosity on the polar scale is increased, and with it the surface accessible to gas.

Obviously, oxygen cannot serve in the case of silica the same useful purpose that it does for charcoal during activation, and to break down the silica polymer dependence has to be placed on water. The preparation of silica from the hydrogel by heating involves the driving off of large proportions of water, different proportions being expelled as the temperature is raised by given increments. As much, if not most, of this water is chemically combined with the silica, exsiccation will tend to break up the polymers. The last modicum of moisture is held with great tenacity, and is only driven away at a temperature exceeding  $700^{\circ}$  C. No. 9, Table I, for example, was one which had not been raised to this temperature, and it therefore held the residual moisture in combination. As a means of activation, the expulsion of water from silica is much less effectual than the heating and partial oxidation of charcoal; the latter method gains by the fact that it can be continued for several hours or days.

The influence of heat upon colloidal silica, apart from the effect of dehydration just referred to, has certain points of interest. A silica which has been imperfectly cleansed of sodium chloride will, on heating, fuze into a glass of negligible adsorptive capacity. A silica chemically clean of chloride, but which was adulterated in the sol stage with carbonaceous matter, as, for example, with seaweed sol, will, if heated above  $750^{\circ}$  C., yield considerable volumes of carbon dioxide, carbon monoxide, and hydrogen through the interaction of the residual moisture and the carbonaceous matter. A chemically clean silica of very high capacity at low temperature, if heated by the blowpipe for a few minutes *circa*  $900^{\circ}$  C. so as to drive off most of the residual water, is not affected in its capacity for nitrogen at liquid air temperature; but, if the same silica be kept in the electric furnace

for five or six hours at  $1000^{\circ}\text{C}$ ., its adsorptive power is destroyed, and, if heated for a few hours at  $750^{\circ}$  to  $900^{\circ}\text{C}$ ., it loses a considerable part of that power. We have here an example of an activated substance being de-activated by prolonged heating. The bearing of this result upon the problem of gas adsorption has already been discussed.

I desire to acknowledge the valuable help given by Messrs. J. Mallinson, B.Sc., and W. Cooper, M.A., B.Sc., in obtaining the experimental data upon which this paper is based, and also the services of Mr. J. J. Brodie in keeping the laboratory supplied with liquid air.

### *Summary.*

Section 2.—The method of determining the adsorptive capacity of a substance at liquid air temperature is described, and results are given of the capacity of silica and certain charcoals.

Section 3.—Charcoal and silica are compared, especially as relates to nitrogen and hydrogen, to illustrate preferential adsorption and to exemplify the influence of chemical composition on gas adsorption.

Section 4.—The effect of the compressibility of the initial layer, when the density of an adsorbent is determined by the immersion method, is considered. An evaluation is made of (*a*) the volume of solid matter, (*b*) that of the interstitial space between the granules, and (*c*) that of the internal gaseous space for silica and cocoanut charcoal.

Section 5.—The density of the nitrogen adsorbed at  $-190^{\circ}\text{C}$ . by silica and charcoal is calculated from experimental data. From these results it becomes possible roughly to estimate the error affecting the density of charcoal ascertained from water immersion, and it is concluded that that method gave a result for the writer's cocoanut charcoal which was at least 0.55 too high. The conditions affecting adsorption at low and high saturation are set forth.

Section 6.—The presence of capillaries is not sufficient to account for adsorption. A high capacity silica may be de-activated, and in the inactive state it remains porous. Graphite, which has no pores, adsorbs gas at  $-190^{\circ}\text{C}$ . The evidence leads to the conclusion that de-activated silica is vitreous. It is argued that a vitreous solid, like a crystal, is a polymer, *i.e.*, a complete atomic linkage. The importance of distinguishing between the coarser capillaries or canals and the finer interpolymeral openings of an adsorbent is emphasised.

Section 7.—Activation is considered to be the effect of disrupting the solid polymers, and the means of accomplishing the partial depolymerisation of charcoal and silica is described.

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*On the Transmission Colours of Sulphur Suspensions.*

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*1. Introduction.*

In the 'Proceedings of the Royal Society,'\* Keen and Porter described some interesting optical effects exhibited by suspensions of 'finely-divided sulphur, obtained by adding dilute sulphuric acid to a weak solution of sodium thiosulphate. As is well known, the solution (which is at first perfectly transparent) becomes turbid when the particles form in it, and the transmission of light by the suspension gradually diminishes in intensity. The colour of the transmitted light, which is at first white, also changes, becoming yellow, orange, red, and then deep crimson red. Finally, the solution (if in a sufficiently thick layer) becomes almost completely opaque. This had been previously supposed to terminate the sequence of phenomena. Keen and Porter observed, however, that after further lapse of time, light begins again to be transmitted by the suspension, the colour of the light which passes through being at first indigo, then blue, blue-green, greenish-yellow, and finally again white. This remarkable reappearance of the transmitted light was quantitatively studied by them, measurements being

\* Ser. A, vol. 89, p. 370 (1914).

made of the intensity of the transmitted light in the various stages of the experiment, red and blue glass plates being used to approximately monochromatise the light of the source. Keen and Porter published curves showing the fraction of the incident light which is transmitted as a function of the time, and found that the shape of the curve is different for different parts of the spectrum, which is of course to be expected, in view of the colours exhibited by the solution when the incident light is white. The diameter of the sulphur particles was also found to increase with time. No attempt was, however, made to explain the observed phenomena on theoretical principles.

The problem was then taken up by the late Lord Rayleigh,\* who attempted to investigate the effects on the basis of the mathematical theory of the scattering of light by small transparent spheres. The explanation of the phenomena observed in the earlier stages of the experiment presented no difficulty. As the particles grow in size, the suspension refuses to transmit, first the shorter waves, and then, finally, the whole visible spectrum. This is precisely what is to be expected, in view of the fact that the scattering power of the particles grows rapidly as their size in relation to their wave-length increases and the transmitting power of the suspension decreases *pari passu* with the increase in the proportion of the energy scattered. Lord Rayleigh did not, however, find it possible to explain the reappearance of the transmitted light in the later stages studied by Keen and Porter, and he went so far as to suggest that there might be some doubt whether the effect was really due to transmitted light in the technical sense of the term.

The present authors have thought it worth while, in view of Rayleigh's remarks, to repeat the experiments, and have obtained results confirming those of Keen and Porter. It is found that the suspension does, indeed, after a certain stage in the growth of the particles, begin again to transmit light regularly, in the strictest optical sense of the term. This is shown by the observation that the coloured light passing through is capable of forming sharply defined optical images. Further, as has already been remarked by Keen and Porter, the effects are not peculiar to sulphur suspensions, but have also been observed in other cases.† The phenomena are thus undoubtedly genuine, and demand an explanation.

It should be remarked, however, that there is a discrepancy between the dimensions of the particles as given by Keen and Porter, and as observed by

\* 'Roy. Soc. Proc.,' A, vol. 90, p. 219 (1914).

† Abney, 'Phil. Trans.,' Part II, p. 653 (1880) ; W. Ritz, 'Comptes Rendus,' vol. 143, p. 167 (1906).



us at the different stages of the experiment. We find that, at the stage of minimum transparency, the diameters of the particles range from  $0.7\ \mu$  to  $0.9\ \mu$ , and, later, increase in the stage of reappearance of the transmitted light from  $1.0\ \mu$  to  $1.3\ \mu$ .\*

It is proposed in the present paper to show how the phenomena described by Keen and Porter may be very simply and quantitatively explained on theoretical principles.

## 2. *The Theory of the Colours.*

The vanishing and subsequent reappearance of the transmitted light (shorter wave-lengths first, longer wave-lengths afterwards), with the increase in the size of the suspended particles, is seen to follow as a natural consequence of theory when we consider the manner in which the attenuation of the light in passing through a turbid medium occurs.

Consider the passage of a plane wave-front through a thin layer of the medium containing  $n$  scattering particles per unit volume. We may, following Rayleigh,† divide the wave-front into elementary areas, in accordance with the Fresnel-Huyghens principle, the effect of the secondary waves diverging from these elements at an external point, P, being integrated to find the amplitude and phase of the transmitted wave. In the present case an appreciable part of the area of the wave-front is occupied by the scattering particles, which are supposed to be sufficiently numerous and irregularly arranged. We have to consider this part separately from the rest of the wave-front. The attenuation of the light in passing through the medium is, according to this procedure, seen to be due to two causes:— (1) the decrease in the area, and consequently also of the resultant effect of the undisturbed portion of the wave-front; and (2) the interference with this of the light scattered in the direction of the primary wave by the particles lying in the wave-front.‡

In the case of the very finest particles, the effect contemplated in (1) is very small, and the phase of the scattered waves in relation to that of the

\* The figures given by Keen and Porter are much larger and appear to be incorrect. The figures noted above represent the average size of the bulk of the particles, but there are many both smaller and larger.

† 'Scientific Papers,' vol. 4, p. 399.

‡ A question may be raised whether *multiply-scattered* light should not also be taken into account in this connection. In reference to this, it may be pointed out that the investigation given below does take this into account in so far as the effect of light reaching the given stratum in the direction of propagation after scattering by the layers *preceding* it is concerned, and this is the only portion of the multiply-scattered light which is in permanent phase-relation with the primary wave and need be taken into account for our present purpose.

primary waves is such that the interference effect referred to in (2) does not (to a first approximation) alter the amplitude of the resulting effect, but only affects its phase.\* With increasing size of the particles, however, the case is altered. The effect (1) becomes considerable, and results in a continuous decrease in the transparency of the medium with increasing size of the particles, the number being assumed to be the same. The amplitude of the light scattered by individual particles also increases rapidly at the same time, and the importance of the effect (2) is therefore enhanced; but whether this results in an increase or decrease of the amplitude of the transmitted wave obviously depends on the phase relationship between the primary and scattered waves in the direction of regular propagation. If the phase of the scattered waves lags sufficiently behind that of the primary waves, we may have actually an increase in the resulting transmission of the light by the suspension with increased size of the particles. As we shall see presently, this is what actually happens.

In order to calculate the amplitude and phase of the secondary waves scattered in the direction of the primary wave, by the dielectric particles, we utilise the formulæ given by Prof. Love as corrected by Rayleigh.† For the case in which the refractive index of the particles is 1.5, the numerical values have been computed by Rayleigh, the ratio of the circumference of the particles to the wave-length having the series of values 1, 1.5, 1.75, 2, and 2.25. The relative refractive index of sulphur particles in water being 1.95/1.33 is sufficiently near to 1.5 for us to accept Rayleigh's numerical values as approximately applicable in the present case. From the Table given by Rayleigh it is seen that the amplitude of the scattered wave in the direction of the primary is independent of the plane of polarisation (as is of course to be expected *a priori*), and increases continually and rapidly with the size of the particles. For our purpose, we require also the numerical values for the case of much larger particles than those used in Lord Rayleigh's calculations. The numerical calculations are extremely tedious but have fortunately been already carried out by one of us (Bidhubhusan Ray) for a ratio circumference/wave-length = 5 in connection with an investigation (which is being separately published) "On the Colour and Polarisation of the Light Scattered by Sulphur Suspensions." Utilising this result in conjunction with the calculations of Rayleigh, the graphs in figs. 1 and 2 have been drawn

\* In this case, the attenuation has been calculated by Rayleigh by an indirect method, depending on the determination of the energy of the waves scattered by individual particles. As to the validity of this process when the particles are larger in size, we shall have some remarks to offer later in the course of the paper.

† 'Roy. Soc. Proc.,' A, vol. 84, p. 30 (1910).

showing the amplitude and phase of the scattered waves as a function of the ratio circumference/wave-length for sulphur particles in water.

We are now in a position to write down the expression for the coefficient of transmission of light through the suspension. Assuming the amplitude of the primary vibration to be unity, the expression for the scattered disturbance due to a single particle in a direction nearly coinciding with  $\theta = 180^\circ$  is

$$A\lambda/2\pi r \cdot \cos 2\pi/\lambda \cdot (ct-r-\delta)$$

where  $A$  and  $\delta$  determine respectively the amplitude and phase.

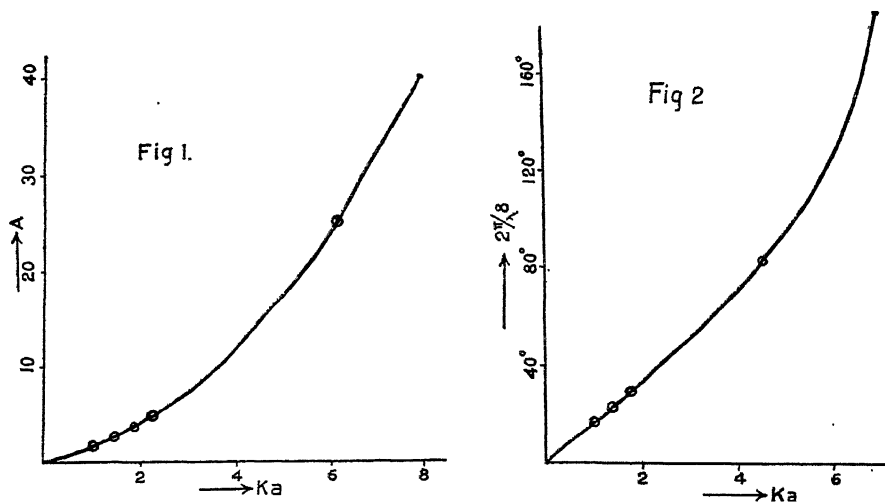


FIG. 1.—Amplitude of scattered wave as a function of  $ka$ .

FIG. 2.—Phase of scattered wave as a function of  $ka$ .

The particles in the stratum are irregularly arranged, but in the direction of the primary wave-propagation, the secondary waves diverging from the particles are in agreement of phase and can accordingly combine to build up a plane wave-front. The amplitude and phase of this plane wave may be found by integration of the effects of the particles in the stratum in the manner adopted by Rayleigh in his papers on the theory of the light of the sky. The resultant at  $P$  of the scattered vibrations which issue from the stratum  $dx$  is

$$\begin{aligned} n d x \lambda / 2 \pi \cdot \int_0^{\infty} A / r \cdot \cos 2 \pi / \lambda \cdot (c t - r - \delta) \cdot 2 \pi z d z \\ = n d x \lambda / 2 \pi \int_x^{\infty} A / r \cos 2 \pi / \lambda \cdot (c t - r - \delta) 2 \pi r d r. \end{aligned}$$

In accordance with the usual procedure, the integral is assumed to vanish at the upper limit and reduces to

$$n d x \lambda^2 A / 2 \pi \cdot \sin 2 \pi / \lambda \cdot (c t - x - \delta), \quad (1)$$

A is here the amplitude of the scattered wave due to a particle in the direction of propagation.

The expression for the primary wave is

$$\cos 2\pi/\lambda \cdot (ct-x). \quad (2)$$

Adding (1) and (2) we find that the coefficient of  $\cos 2\pi/\lambda \cdot (ct-x)$  is thus altered by the particles in the layer  $dx$  from 1 to

$$(1 - An dx \lambda^2 / 2\pi \cdot \sin 2\pi/\lambda \cdot \delta)$$

and the co-efficient of  $\sin 2\pi/\lambda \cdot (ct-x)$  from 0 to  $An dx \lambda^2 / 2\pi \cdot \cos 2\pi/\lambda \cdot \delta$ .

The diminution  $dE_1$  of energy of the primary wave due to the interference with the scattered waves is therefore

$$\frac{dE_1}{E} = -An dx \lambda^2 / \pi \cdot \sin 2\pi/\lambda \cdot \delta.$$

The diminution  $dE_2$  due to reduction in the effective area of the undisturbed wave-front is given by  $dE_2/E = -2na^2\pi dx$ , where  $a$  is the radius of a particle. The total diminution

$$dE/E = (dE_1 + dE_2)/E = -(2n\pi a^2 + An\lambda^2/\pi \cdot \sin 2\pi/\lambda \cdot \delta) dx.$$

The effect of passage of the wave through the successive strata of the turbid medium may be found by integration. We have thus

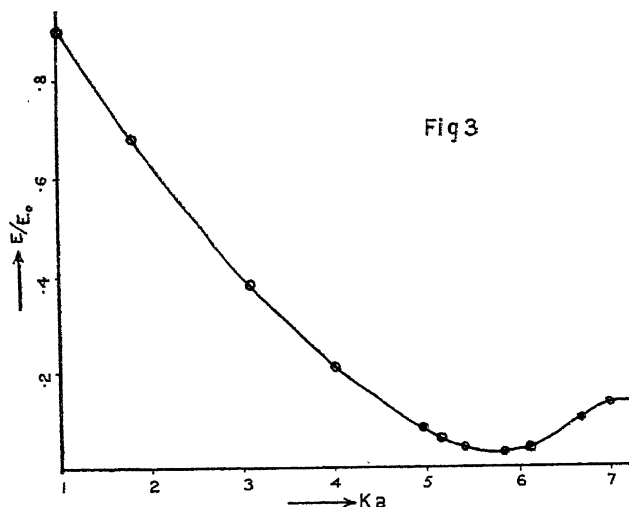
$$E = E_0 e^{-(2\pi a^2 + A\lambda^2/\pi \cdot \sin 2\pi/\lambda \cdot \delta) nx}, \quad (3)$$

where  $x$  is the total thickness. Since the process of integration considers the effect on the transmitted wave arriving at any given stratum of its passage through all preceding strata, the investigation takes into account the influence of multiply-scattered light so far as is relevant to our present purpose, as remarked previously in a footnote. In arriving at the foregoing result, we have tacitly assumed that all the particles are of the same size. In the actual experiment, the size of the particles is variable to some extent, but by taking the effective average size we may obtain a sufficient approximation to the truth; if desired, there would be no difficulty in modifying the formula to obtain a more accurate result by considering separately the effects of particles of different sizes in groups and superposing them to find the resultant.

In applying the formula (3) to the actual conditions of the experiment, it must be remembered that, as the precipitate of sulphur gradually forms, both the average size of the particles and their number per unit volume may vary. A change in the number  $n$  would increase or decrease the transmission-coefficient for all wave-lengths simultaneously, whereas the characteristic feature observed in the experiment is the reappearance of the shorter wave-lengths first and of the longer wave-lengths afterwards. The increase in the

effective average size of the particles is thus the more important factor in the observed results.

By actually counting,  $n$  is found to be of the order  $1.5 \times 10^8$  per cubic centimetre. Taking the value of  $A$  and  $\delta$  from the graphs in figs. 1 and 2, and the thickness  $x$  of the liquid to be 1 cm., the graph in fig. 3 has been



drawn, showing the fraction  $E/E_0$  of the light transmitted as a function of the radius  $a$  of the particles. It is seen from the graph that there is an augmentation of transparency when the circumference of the particle is about  $6\lambda$ . With a greater thickness of the liquid, the failure of transmission and its reappearance at a later stage is even more clearly noticeable. These results are in agreement with observation.

### (3) *Concluding Remarks.*

Reference should be made here to the apparent paradox that, though the energy of the waves *scattered* by an individual particle increases continually with its size, nevertheless, the proportion of the energy of the incident light, regularly transmitted by a medium containing a large number of such particles in suspension, may also increase at the same time. This seems at first sight repugnant to the principle of conservation of energy. The paradox is, however, real only if we assume that the energy of the light scattered by  $n$  such particles in a unit volume increases *pari passu* with the increase of the energy scattered by an individual particle present in an otherwise homogeneous medium. Such an assumption is not justified, at least in the present case, as it ignores the permanent phase-relationship and

consequent capacity for interference of the scattered and primary waves in the original direction of propagation. The difficulty felt by Rayleigh in explaining the phenomenon studied by Keen and Porter really arose from the tacit assumption made by him that an increase in the energy scattered by an individual particle necessarily connotes an increase in the energy scattered by a medium containing a large number of such particles.

Further, the observed *increase* in the power of transmission of light by the turbid medium at a certain stage necessarily involves on the principle of conservation of energy, a *decrease* in the proportion of energy scattered by it at the same stage. In other words, when a steady parallel beam of light passing through a cell containing the sulphur suspension is focussed on a screen, at the stage at which the transmitted light reappears, there should be a distinct diminution in the intensity of the scattered light also falling upon the screen. The effect to be expected is, however, rather small, and may easily escape observation.

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*The Photographic Efficiency of Heterogeneous Light.*

By F. C. Toy, M.Sc., A.Inst.P.

(Communicated by Prof. A. W. Porter, F.R.S. Received May 12, 1921.)

There are some sources of illumination which are much more active photographically than others, and one of the most active of all artificial sources is the mercury vapour lamp. The energy of the radiation from this lamp is concentrated in a comparatively few spectral lines, and most of these are in that region of the spectrum which is the region of greatest absorption by the silver halide grains of which the photographic emulsion is composed. This, in itself, may be the complete explanation of the intense photographic activity of this particular illuminant, but the question arises as to whether the explanation is, in part, merely the fact that the light is concentrated into a few wave-lengths, apart altogether from any consideration of the absorption coefficient. In other words, a given quantity of radiant energy absorbed in the grains may give a greater photographic effect when it is all of one frequency than when it is a complex radiation such as white light. The object of the present paper is to discuss this question in the light of recent researches on the photographic plate.

This idea has recently been brought forward by Slade and Higson\* with

\* 'Roy. Soc. Proc.,' A, vol. 98, p. 154 (1920).

special reference to the application of the Quantum Theory. They have suggested that when the photographic plate is illuminated by heterogeneous light, radiations of different frequencies act independently, *i.e.*, they do not reinforce one another in producing the photochemical effect, and that white light may be considered as consisting of an enormous number of such independent monochromatic radiations. That is to say, the probability of a grain being changed depends not only on the total energy absorbed, but also on the number of different kinds of energy of which that total is composed.

If this theory is correct, the extent to which it effects the efficiency (*i.e.*, the ratio of the photographic effect to the intensity of the light producing it) of any given light will depend on the form of the law connecting the effect ( $A$ ) with the intensity of the light ( $I$ ).

Consider the following operations in which the conditions of exposure, development, etc., are always the same.

(*a*) The intensity of  $n$  different monochromatic radiations are so adjusted that when they act separately they each produce on the photographic plate the same effect.

(*b*) The intensity of each radiation is reduced to  $1/n$ th its original value (as measured by a thermopile) and the plate illuminated by all the  $n$  radiations simultaneously. Two possible laws of action may be distinguished as follows:—

(1) All radiations may act simultaneously, but independently, *i.e.*, each acts as though the others are not present.

(2) All radiations may act simultaneously but not independently.

For the sake of clearness we will denote by suffix  $s$  all quantities relating to class (*a*), by suffix  $i$  those relating to (*b* 1) and by suffix  $r$  those relating to

(*b* 2) Consider first what the effect will be if  $A$  varies as  $I$ .

Operation (*a*) will give the equations:—

$$A_s = k_1 I_1 = k_2 I_2 = \dots k_n I_n.$$

Operation (*b*) will give, if (*b*, 1) is correct

$$A_i = \Sigma k_1 I_1 / n = A_s.$$

or, if (*b*, 2) is correct

$$A_r = K_0 \Sigma I_1 / n,$$

which may or may not be equal to  $A_s$ , depending on the value of  $K_0$ . If, however,  $A$  is not proportional to  $I$ ,  $A_i$  is not equal to  $A_s$ . Now Slade and Higson have shown that the relation between the light intensity,  $I$ , and the effect produced,  $A$ , is given by

$$A = \alpha I (1 - e^{-\epsilon I}), \quad (1)$$

where  $\alpha$  and  $\beta$  are constants, so that, if the intensity is small,  $A$  varies as  $I^3$ . When this is the case, operations (a) and (b) will give

$$\begin{aligned} A_s &= k_1 I_1^2 = k_2 I_2^2 = \dots = k_n I_n^2 \\ A_i &= \Sigma k_1 I_1^2 / n^2 = A_s / n \\ A_r &= K_0 (\Sigma I_1)^2 / n^2. \end{aligned} \quad (2)$$

The value of  $A_r$  and the relation between  $A_r$  and  $A_s$  need not be considered further in the present paper, for equation (2) provides a crucial test of the theory of independent action. It states that, if the radiations act independently, and  $A$  is a quadratic function of  $I$ , then the effect produced by each radiation separately is  $n$  times as large as that which is produced when they all act together, each with an intensity of  $1/n$ th its original value. This point can be tested experimentally.

Silberstein and Sheppard\* have recently criticised the validity of equation (1), on the ground that the experimental evidence is not sufficiently complete. Since the argument that has been developed is based essentially on this particular form of  $f(I)$ , the author has taken the precaution of investigating this independently, and has confirmed, beyond all reasonable doubt, this result of Slade and Higson. In Table I, values of  $A$  found experimentally are compared against the values as calculated from the empirical equation

$$A = 2.25 I (1 - e^{-2.5 I})$$

obtained by putting  $\alpha = 2.25$  and  $\beta = 2.5$  in equation (1), and in every case excellent agreement is found.

Table I.

Relative intensity.	A (obs.).	A (calc.).	Relative intensity.	A (obs.).	A (calc.).
1.4	3.07	3.06	0.7	1.31	1.30
1.3	2.83	2.81	0.6	1.05	1.05
1.2	2.59	2.57	0.5	0.80	0.81
1.1	2.35	2.31	0.4	0.57	0.56
1.0	2.08	2.07	0.3	0.37	0.36
0.9	1.83	1.84	0.2	0.19	0.18
0.8	1.57	1.56	0.1	0.06	0.05

In all experiments that were made only two different colours were used (*i.e.*,  $n = 2$ ), and the difference of frequency between them was about 300 Å. The apparatus which was designed for this work has already been fully described elsewhere,† so that it is only necessary to refer to it briefly

\* 'Phot. Jour.', vol. 61, p. 205 (1921).

† 'Phot. Jour.', vol. 61, p. 176 (1921).



here. In principle, it is much the same as the monochromatic illuminator designed by Sir William Abney, and described in his book entitled "Researches in Colour Vision." The spectrum of the light source is first formed by means of the ordinary prism spectroscope. In the plane in which this spectrum is focussed is an arrangement of two adjustable slits, by means of which any desired spectral ranges may be isolated. An auxiliary lens, placed immediately after the slits, projects on to the photographic plate an enlarged image of a face of the prism, the colour of the image depending on the position of the slits. Its intensity depends on its area and on the quantity of light transmitted, the slits being so designed that the more intense beam can be cut down to any desired extent. The plate is held in a special holder, and the photographs are taken through a small rectangular opening about  $1 \times 0.5$  cm., so that several exposures can be made side by side on the same plate.

For the higher intensities, the blue and violet lines of the mercury arc were used, and, for the lower intensities, two narrow strips of a continuous spectrum, with approximately the same difference of frequency. All the intensities were low enough to be on the  $I^2$  portion of the curve. The method of experiment was as follows:—The intensities of the blue and violet were first adjusted, by means of slits, until the effect produced (determined by counting the number of grains developed) on adjacent sections of the same photographic plate by either colour exposed separately, was exactly the same under the same conditions of exposure, development, etc. The intensity of each radiation was then halved (by doubling the area of the image), and a third section of the same plate was exposed for the same time, with both colours illuminating the plate simultaneously. The intensity was varied over a very large range, from a maximum such that nearly half the grains were made developable in about two minutes to a minimum so low that less than 20 per cent. of the grains were changed in an exposure of fifteen hours.

According to the theory, if these two colours act independently of one another in producing the effect on the plate, we should expect in the third exposure to obtain only about one half the effect produced by either colour separately. Some typical examples are shown in Table II. It is clear that there is not the slightest evidence to show that the two colours did not reinforce one another, for the same effect (within limits of experimental error) was produced whether the light was blue or violet only or a mixture of half of each. The variations from exact equality are accounted for by a slight inconstancy in the intensity of the light source during the exposures:—

Table II.

Light source.	Time of exposure.	Photographic effect.		
		Blue only.	Violet only.	$\frac{1}{2}$ Blue + $\frac{1}{2}$ Violet.
Mercury arc .....	2 minutes	0·47	0·45	0·41
Mercury arc .....	2 minutes	0·47	0·48	0·41
Metal filament lamp .....	3 hours	0·35	0·35	0·40
	48 minutes			
Metal filament lamp .....	15 hours	0·17	0·18	0·18

It may be concluded, therefore, that over the spectral range used in these experiments radiations of different frequencies do not act independently in producing the photochemical change, but probably simply as a total amount irrespective of any difference in quality.

It is difficult to imagine how the theory which has been discussed could be valid unless it is supposed that the molecules contain an enormous number of oscillators each vibrating simply harmonically with a slightly different period and each responding only to a particular frequency in the incident light. This would imply that the atom contained as many different kinds of oscillators as there are homogeneous trains into which the spectrum can be resolved. There is no evidence to support such a view of atomic structure.

In conclusion, the author wishes to express his thanks to the Director of Research of the British Photographic Research Association, Dr. T. Slater Price, for his interest in this work, and to Prof. A. W. Porter for much valuable criticism.

*Experiments with Rotating Fluids.*

By G. I. TAYLOR, F.R.S.

(Received June 22, 1921.)

[PLATE 2.]

It is well known that predictions about fluid motion based on the classic hydrodynamical theory are seldom verified in experiments performed with actual fluids. The explanation of this want of agreement between theory and experiment is to be found chiefly in the conditions at the surfaces of the solid boundaries of the fluid.

The classical hydrodynamical theory assumes that perfect slipping takes place, whereas in actual fluids the surface layers of the fluid are churned up into eddies. In the case of motions which depend on the conditions at the surface, therefore, no agreement is to be expected between theory and experiment. This class of fluid motion, unfortunately, includes all cases where a solid moves through a fluid which is otherwise at rest.

On the other hand, there are types of fluid motion which only depend to a secondary extent on the slip at the boundaries. For this reason theoretical predictions about waves and tides, or about the motion of vortex rings, are in much better agreement with observation than predictions about the motion of solids in fluids. Some time ago the present writer\* made certain predictions about the motion of solids in rotating fluids, or rather about the differences which might be expected between the motion of solids in a rotating fluid and those in a fluid at rest. These predicted features of the motion did not depend on conditions at the boundaries. It was therefore to be anticipated that they might be verified by experiment. The experiments were carried out and the predictions were completely verified.

In view of the interest which attaches to any experimental verification of theoretical results in hydrodynamics, and more particularly to verifications of those concerning the motion of solids in fluids, it seems worth while to publish photographs showing the experiments in progress. In the second and third part of the paper further experiments are described in which theoretical predictions are verified in experiments with water.

*Motion of Cylinder and Sphere in Rotating Fluid.*

In these experiments a solid cylinder and a solid sphere, of the same density as water, were drawn through a rotating vessel containing water.

\* 'Roy. Soc. Proc.' A, vol. 93, p. 99 (1917).

The threads by means of which these solids were dragged, passed through small rings attached to the vertical wall of the circular rotating glass vessel in which the water was contained. The solids were initially attached to the opposite point of this vessel to that at which the rings were attached. Under these circumstances, if the vessel were not rotating, a symmetrical body like a sphere or cylinder would evidently pass along a diameter through the centre of the apparatus when towed by the threads.

When the vessel was rotating, however, the theoretical prediction\* was that the cylinder would pass through the centre of the apparatus just as if the whole system were not rotating, while a sphere, or any symmetrical three-dimensional body, would be deflected and would pass to one side of the centre. The verification of this prediction was first made in an apparatus with which it was difficult to obtain photographs owing to the difficulty of throwing a light through the water towards a camera placed on the axis of rotation above the apparatus. A new apparatus was therefore devised, in which the vertical central spindle used in the previous apparatus was done away with.

Two dishes in the form of circular cylinders were made. Each had a thin plate-glass bottom, about 1 mm. thick. The diameter of one of them was made about 1/8 inch larger than the other, so that the smaller one would fit inside the larger one, leaving a space of about 1/16 inch all round. The inner dish was filled about two-thirds full of water, and the outer one was filled quite full. The inner cylinder would then float in the outer one. It was driven round a vertical axis by means of a jet of water projected at its outside surface. When the apparatus was set up so as to run truly, it was found that a very uniform rate of rotation would be obtained by this method. The whole apparatus stood in a trough with a plate glass bottom, in which the water which overflowed could be collected. This apparatus is shown in text-fig. 1.

In order to take instantaneous photographs, the apparatus was illuminated from underneath, and a camera with a lens of 15 inches focus was fixed about 6 feet above it. Two methods of illumination were used. In the first method the direct light from a spark between an aluminium wire and a hole in an aluminium plate was focussed, by means of a condenser, on the lens of the camera. In the second method use was made of diffused light, a mercury vapour spark being used to illuminate a ground-glass plate placed close under the apparatus. Plate 2, figs. 1, 2, 5 and 6, were taken by the first method, while figs. 3 and 4 were taken by the second. It is worth pointing out that the apparatus is very simple, and that it is easy to project all the

\* *Loc. cit.*, p. 105.

experiments to be described in this paper on to a screen by means of a lantern.

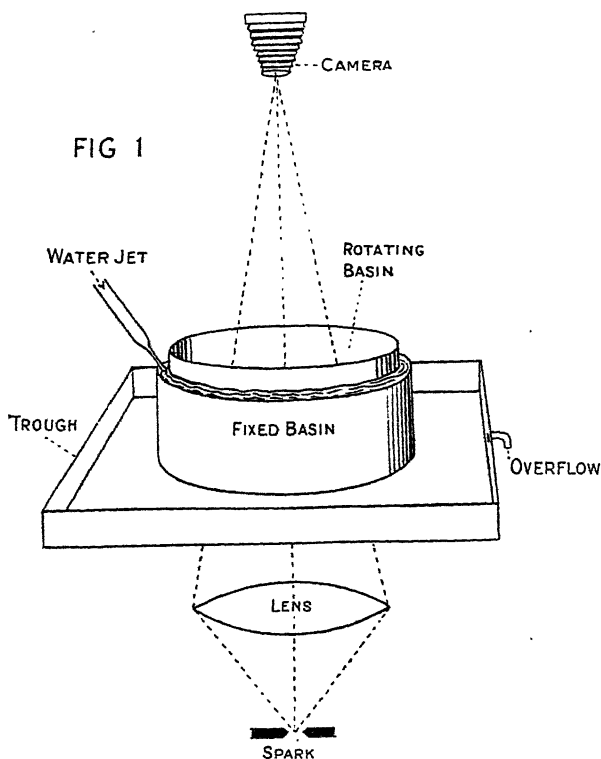


FIG. 1.—General Arrangement of Apparatus.

It was thought at first that it might be difficult to arrange to tow the solids through the rotating basin in such a way that no appreciable variation in the speed of rotation would occur. To avoid this difficulty, the threads used to tow the solids were led from the edge of the apparatus back to the centre, and were pulled upwards from that point. The method adopted for doing this was to fix a transparent celluloid bridge across the basin in such a position that its centre line ran from the initial position of the solid to the point towards which the threads were towing it. This transparent bridge shows up clearly as a broad band in figs. 1 and 2 (Plate 2). The threads passed through a small hole in the centre of the bridge, and were attached to a small wire ring, which rested on it in the middle.

To perform the experiment, the solid, which was usually made of wax or boxwood, was placed on small pins projecting from the side of the trough. The threads were then stretched across the basin to the opposite side, and

led from there up to a ring close under the celluloid bridge. From this point they passed along the underside of the bridge to the centre, where they passed up through the central hole.

The tank was then set rotating, and, when the whole system had attained a constant speed, a steel pricker was inserted into the wire ring, and raised approximately vertically. The sketch (text-fig. 2) shows the apparatus in action. In the case of the cylinder two threads were used to ensure that

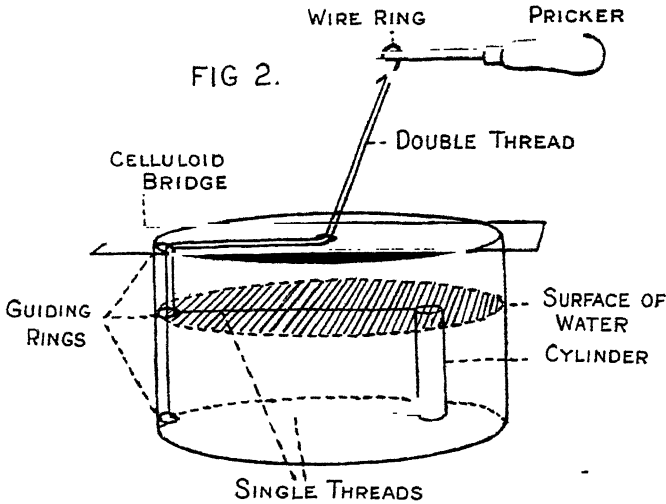


Fig. 2.—Rotating Tank arranged for Experiment with Cylinder.

the axis should remain vertical. This is the case shown in the sketch. With the sphere, only one thread was used.

The results in the two cases are shown in the photographs (Plate 2, figs. 1 and 2). In fig. 1 the cylinder is shown at the middle point of its path. Since its axis is nearly vertical it is seen end-on, and appears therefore as a black circle in the photograph. In the particular experiment shown in fig. 1, the axis of the cylinder had accidentally got tilted very slightly away from the vertical, so that both the upper and lower threads show as two distinct threads. The pricker and wire ring are seen at the bottom of the photograph; they are naturally rather out of focus. The lines in the photograph which are not straight are threads used for drawing the solids in other experiments. They have nothing to do with the present experiment. It will be seen that the predicted result is verified. The cylinder is moving practically straight across under the middle line of the celluloid bridge.

Fig. 2 shows the result in the case of the sphere. In this case it will be seen that the sphere is being deflected through a large angle, so that it is under the edge of the bridge instead of being under the middle, as it was in

the case of the cylinder. It is not moving in the direction in which the thread is pulling it, but is being deflected to the right. In this case the liquid was rotating in the direction opposite to that of the hands of a clock. Again, this is the result which was predicted by theory.

*Motion of Vortex Rings in a Rotating Fluid.*

The difference between two- and three-dimensional fluid motion which has been discussed must apply to all fluid motions. It must therefore apply to the propagation of a vortex ring, as well as to the motions of a sphere and cylinder.

It is impossible, apparently, to produce a two-dimensional analogue of a vortex ring. If such a thing could be produced, it should, according to this theory, propagate itself in a straight line through a fluid, whether the fluid is rotating or not. In other words, since a rotation of the whole system should make no difference to any two-dimensional flow, it should make no difference to the two-dimensional analogue of a vortex ring.

The flow in a vortex ring, however, is three-dimensional, and a rotation of the whole system should affect it. For reasons explained in the paper already referred to,\* it was anticipated on theoretical grounds that if a vortex ring can be propagated in a rotating fluid, it will not move in a straight line relative to the rotating system, but will move in a circle in the *opposite direction* to that in which the whole system is rotating.

In fig. 3 is shown a photograph of a vortex ring which has been projected from a small vortex box immersed in the water.† The basin was not rotating in this experiment. It will be seen that the ring, which is being projected along a diameter of the basin, moves in a straight line, as was to be expected. A short wire was attached to the vortex box, so as to point in the direction in which the ring was aimed. This will be seen in the photograph (fig. 3).

Fig. 4 is a photograph of a vortex ring projected when the whole system is rotating. In this photograph, the predicted curved path traversed by the ring is shown up clearly by the track of coloured fluid left behind during its flight.

The jet which drives the apparatus can be seen on the right-hand side of

\* *Loc. cit.*, p. 107.

† The liquid eventually used was not pure water, but an acid solution of ferrous sulphate. The rings consisted of a solution of permanganate of potash made up to the same density as the ferrous sulphate solution by mixing with a heavy neutral salt. The rings then dissolved after they had broken up and a large number could be projected without discolouring the solution. For the suggestion to use this solution I am indebted to Dr. A. A. Robb.

the photograph. It will be noticed that the basin is being driven in the counter-clockwise direction, and that the vortex ring is going round its circle in a clockwise direction, as predicted theoretically.

One point which the experiments bring out is that the direction of the axis of the ring appears to be fixed in space, so that the ring would go round in a circle once during each revolution of the system. It would therefore be possible to consider the motion as being a steady motion relative to axes whose directions are fixed in space, but whose origin moves and is situated at the centre of the path of the vortex ring.

*Slow Motions in a Rotating Fluid.*

The investigations described above naturally led to inquiries as to whether rotating liquids possess any other properties which can be predicted from hydrodynamical theory. The following striking peculiarity of rotating fluids was discovered in the course of this work. If any small motion is communicated to a fluid which is initially rotating steadily like a solid body, the resulting flow must be two-dimensional, though small oscillations about this state of slow motion are possible.\* This may be proved as follows:—

Let  $u, v, w$  be the components of velocity of any particle of fluid relative to a system which is rotating uniformly with velocity  $\omega$  about the axis of  $z$ .

The circulation round any circuit in the fluid is

$$I = \oint \{ (u - \omega y) dx + (v + \omega x) dy + w dz \},$$

the integral being taken round the circuit.

This may be divided into two parts

$$(a) \quad I' = \oint \{ u dx + v dy + w dz \}$$

which may be called the circulation due to the relative motion, and

$$(b) \quad \oint (-\omega y dx + \omega x dy)$$

which can be expressed in the form  $2\omega A$ , where  $A$  is the area of the projection of the circuit on a plane perpendicular to the axis of rotation.

In a non-viscous fluid the circulation round any circuit which always consists of the same ring of particles, is constant. Hence it will be seen that  $I = I' + 2\omega A$  is constant.

Evidently if the motion relative to the rotating system is small this means that the variations in  $A$  during the whole motion are small. The liquid must therefore move in such a way that the area of the projection of any ring of particles on a plane perpendicular to the axis of rotation is nearly constant.

\* This is practically the same thing as the fact previously noted by Proudman, that small steady motions of a rotating fluid are two-dimensional.



Let us now enquire how this geometrical condition may be expected to reveal itself during the motion. First, we shall see what types of motion are possible in a fluid for which the areas of the projections on a given plane of all possible circuits of particles remain constant during the motion. This condition may be expressed mathematically by writing down an expression for the rate at which the area of the projection increases and equating it to 0. In this way it is found that

$$\int (vdx - udy) = 0,$$

the integral being taken round the circuit.

This expression may be transformed by Stokes' Theorem into the form

$$\iint \left\{ l \frac{\partial u}{\partial z} + m \frac{\partial v}{\partial z} - n \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \right\} dS = 0,$$

where  $dS$  is an element of surface of any surface which is bounded by the circuit in question and  $l, m, n$  are the direction cosines of the normal to that surface.

Since this relation holds for all possible circuits,

$$\partial u / \partial z = 0, \quad \partial v / \partial z = 0, \quad \text{and} \quad \partial u / \partial x + \partial v / \partial y = 0. \quad (1)$$

Hence, since the fluid is incompressible,

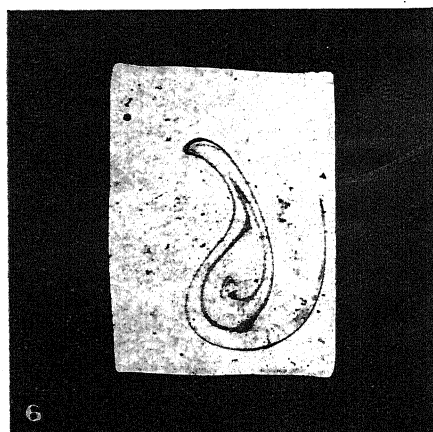
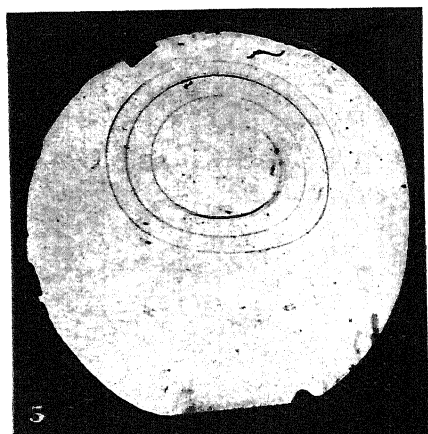
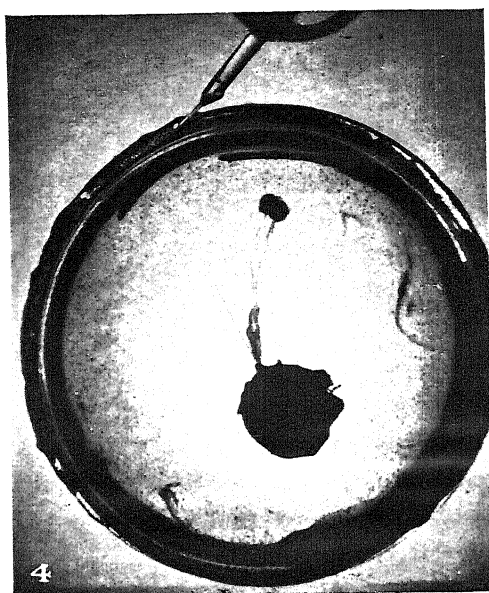
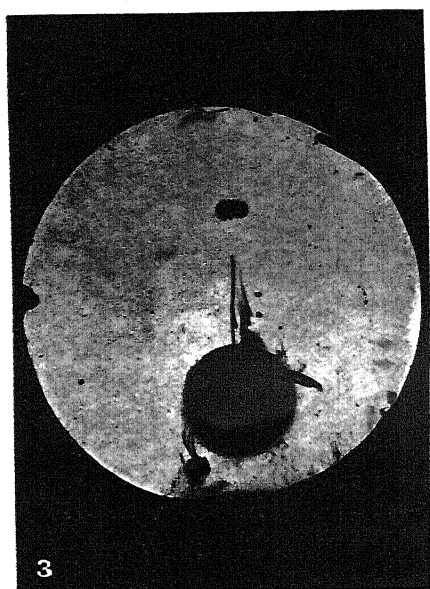
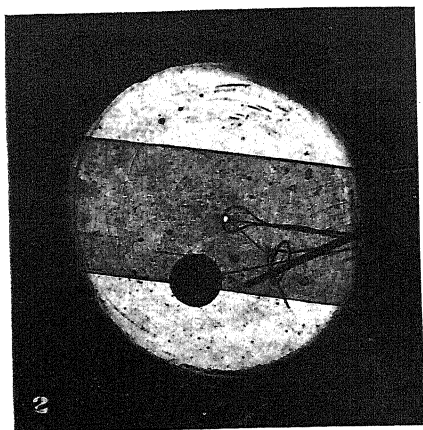
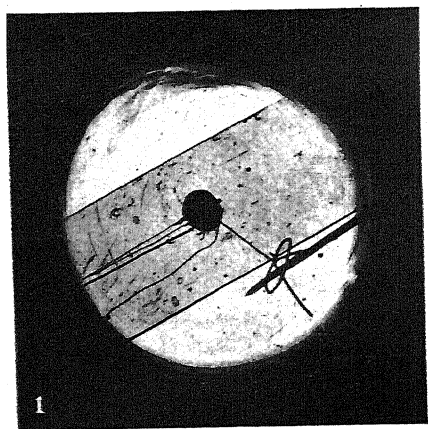
$$\partial w / \partial z = 0. \quad (2)$$

The conditions (1) show that any two particles which are originally in a line perpendicular to the given plane, will always remain in a line perpendicular to it. The condition (2) shows that they also remain at a constant distance apart throughout the motion.

If therefore any small motion be communicated to a rotating fluid the resulting motion of the fluid must be one in which any two particles originally in a line parallel to the axis of rotation remain so, except for possible small oscillations about that position. This property of rotating fluids is found to be true experimentally. It can be demonstrated in a very striking way by means of the apparatus described in the first part of this paper. The liquid is first made to rotate steadily as a solid body. A small motion is then communicated to it, and a few drops of coloured liquid are inserted. However carefully these drops are inserted the volume occupied by coloured water necessarily measures at least half a centimetre in every direction.

The slow movement of the fluid then draws this coloured portion of the fluid out into sheets. These sheets remain always parallel to the axis of rotation. They go on spreading almost indefinitely till they may perhaps be twenty or thirty times as long as the diameter of the basin, their thickness





decreases correspondingly till they are only a small fraction of a millimetre thick.

The accuracy with which they remain parallel to the axis of rotation is quite extraordinary. After the motion has been going on for some time it is only possible to see that the colouring matter is not uniformly diffused through the liquid by placing one's eye on, or near, the axis of rotation. The portion of the fluid which is passing immediately beneath the eye then appears to be filled with fine lines which are, of course, in reality, thin sheets seen edgewise.

The photographs shown in figs. 5 and 6 were taken by a camera placed accurately on the axis of rotation of the basin. It will be seen that the lines are extremely fine. The sheets into which the originally diffuse patch of coloured liquid are drawn are therefore extremely thin, and are moreover accurately parallel to the axis of rotation. It appears therefore that in this case also the theoretical prediction is completely verified by experiments with real fluids.

In fig. 5 the small motion was communicated to the fluid by changing the speed of the rotating basin temporarily. Fig. 6 shows an experiment in which a rectangular boundary was placed in the rotating basin in order to alter the effect produced by a change of speed, and so produce a different pattern.

In a future paper the author hopes to discuss what happens in the case when the boundaries of the fluid move slowly in such a way that three-dimensional motion must take place.

#### DESCRIPTION OF PLATE.

- Fig. 1.—Cylinder passing under centre of tank, seen from point above the tank and on the axis of rotation.
- Fig. 2.—Sphere being deflected, seen from the same point as the cylinder shown in fig. 1.
- Fig. 3.—Vortex ring being projected in a non-rotating tank. The large black disc is the vortex box, seen end-on. The wire seen projecting from the box indicates the direction of projection of the ring. The ring will be seen clear of the end of the wire.
- Fig. 4.—Vortex ring projected in rotating tank. The curved path is shown by the trail of coloured liquid left by the ring in its flight. The jet which drives the inner basin is seen at the top of the photograph.
- Fig. 5.—Sheet of coloured liquid seen from a point on the axis of rotation in a rotating liquid.
- Fig. 6.—Another sheet of coloured liquid. In this case the liquid is contained in a rectangular boundary.
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*On certain Geological Effects of the Cooling of the Earth.*

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1. *The Thermal History of the Earth.*

The former molten state of the earth has been widely accepted as an important and fruitful hypothesis in physical geology ever since the enunciation of Laplace's theory of the origin of the solar system. Elie de Beaumont, followed by other investigators, suggested that the cooling and consequent contraction of the crust was a potent cause, and probably the chief cause, of the horizontal compression that led to mountain building. The theory was put into quantitative form by C. Davison\* and Sir G. H. Darwin,† their numerical data being taken from Lord Kelvin's theory of the cooling of the earth. Osmond Fisher‡ objected to this that the compression they found was inadequate to account for existing mountain chains, but neither he nor those geologists who have followed him appear to have given an estimate of any significance of the amount of compression actually needed. Such an estimate, admittedly rough and provisional, but probably correct in order of magnitude, was made by the writer in a paper§ in the 'Philosophical Magazine' for 1916. At the same time, I used Holmes's data|| about the age and thermal properties of the earth in preference to Kelvin's, and found that with these the available compression appeared to be sufficient.

According to the form of the tidal theory of the origin of the solar system, developed by Chamberlin and Moulton in their Planetesimal Theory, the earth became solidified by adiabatic expansion immediately on its ejection from the sun, and in its subsequent growth by accretion never attained fusion temperature; so that we have to contemplate an earth that has always been solid, and cannot have cooled to anything like the extent that was implied by the older theory. I believe, however, that this supposition is erroneous. It is at least probable that most of the matter that went to form the earth came from the superficial regions of the sun (if the encounter with the passing star was "slow" in Jeans's sense, the whole of it would), and that, when it gathered together, the relative increase in

\* 'Phil. Trans.,' A, vol. 178, pp. 231-242 (1887).

† 'Phil. Trans.,' A, vol. 178, pp. 242-249 (1887); or 'Scientific Papers,' vol. 4, p. 354.

‡ 'Physics of the Earth's Crust,' Macmillan, 1889.

§ "The Compression of the Earth's Crust in Cooling," 'Phil. Mag.,' vol. 32, pp. 575-591 (1916).

|| 'Geological Magazine,' March, 1915, pp. 102-112.

the depth was greater than the relative diminution in gravity. If this were so, the average pressure inside this matter would be greater than before instead of less, and the temperature would rise on ejection instead of falling, even if the change was adiabatic. Again, even if it were shown that the mean pressure would fall, adiabatic cooling below the boiling point could be caused only by evaporation, and therefore would not lower the temperature below a point at which the vapour pressure was insignificant. Thus the temperature could never be reduced in this way by more than  $200^{\circ}$  C. at most below the boiling point. But the difference between the melting and boiling points of the substances concerned is at least several hundred degrees. Hence the primeval earth, if adiabatic cooling took place at all, could at most have cooled to the liquid state and not to the solid state. Solidification must have taken place later and more gradually in consequence of radiation.

As I have shown in a previous paper,\* accretion of small particles to such an extent as to be of cosmogonical importance is impossible, since the mutual impacts of the particles would volatilise them before any important growth could take place. Accordingly, we must suppose that at an early stage in the history of the earth it was liquid at the surface, and that subsequent development took place by radiative cooling without much mechanical interference from outside. The theory of a formerly molten and cooling earth is therefore implied by the tidal theory of the origin of the solar system, which, on astronomical grounds, is the most acceptable yet advanced.†

In the present paper I develop certain consequences of the cooling of the earth that have not yet been dealt with. In the first place, however, some discussion of the earth's thermal history is necessary.

The problem of the flow of heat in a solid depends on the differential equation

$$\frac{\partial V}{\partial t} - \frac{k}{\sigma \rho} \left( \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} \right) = \frac{P}{\sigma \rho}, \quad (1)$$

where  $V$  is the temperature,  $t$  the time,  $x$ ,  $y$  and  $z$  the three Cartesian position co-ordinates,  $k$  the thermal conductivity,  $\rho$  the density,  $\sigma$  the specific heat, and  $P$  the number of calories generated in unit time by radio-activity or chemical change in unit volume of the solid. In the present problem the changes in temperature are confined to the superficial layers,

\* 'Monthly Notices of Roy. Astron. Soc.,' vol. 77, pp. 84-112 (1916).

† J. H. Jeans, 'Problems of Cosmogony,' Camb. Univ. Press, 1920; H. Jeffreys, "The Early History of the Solar System," 'Monthly Notices of R.A.S.,' vol. 78, pp. 424-441 (1918).

whose thickness is small compared with the radius of the earth. Accordingly, if we take the axis of  $x$  to be vertically downwards, the equation reduces to

$$\frac{\partial V}{\partial t} - h^2 \frac{\partial^2 V}{\partial x^2} = \frac{P}{\sigma \rho}, \quad (2)$$

where  $h^2$  has been written for  $k/\sigma\rho$ . Let some particular integral of this differential equation be  $V_0$ . As a rule,  $P$  is, with sufficient accuracy, a function of  $x$  alone, so that a particular integral is  $-\iint P/kdxdx$ . Whether it is or not, however, provided only that a particular integral can be found, we have only to find a solution of the differential equation (with  $P$  on the right put equal to zero) which will reduce when  $t$  is zero to  $f(x)$ , where the initial temperature is given to be  $f(x) + V_0$ , and which will satisfy the appropriate condition at the surface of the earth.

In the present problem the initial temperature is specified from  $x = 0$  to  $x = \infty$ ; it is to be derived from the physical conditions at the time of the solidification of the earth. It is easy to show from known data that the amount of heat arriving at the surface of the earth by conduction from the interior is a very small fraction of that obtained by radiation from the sun, and hence that the surface temperature is determined solely by the condition that the radiation into space from the earth must balance that received from the sun. There is no reason to believe that there has been in geological time any wide variation in either the solar radiation or in the radiative constants of the surface of the earth, and consequently we are justified here in assuming that the variations of surface temperature have not been sufficient to demand their recognition. It will be convenient, therefore, to adopt a constant surface temperature for our zero of temperature. Then we have the surface condition that when  $x = 0$ , the temperature is always zero, except at the initial moment. Now we can, without loss of generality, make the particular integral  $V_0$  one that vanishes with  $x$ . Then  $V - V_0$  still satisfies the equation (2) after zero has been substituted for  $P$ , and is equal to  $f(x)$  when  $t$  is zero. Also, it vanishes when  $x = 0$  for all values of the time. The solution that satisfies all these conditions can be shown to be

$$V = V_0 + \frac{1}{\sqrt{(\pi)}} \int_{-x/2ht}^{\infty} e^{-q^2} f(2qht^{\frac{1}{2}} + x) dq - \frac{1}{\sqrt{(\pi)}} \int_{-\infty}^{-x/2ht} e^{-q^2} f(-2qht^{\frac{1}{2}} - x) dq. \quad (3)$$

This is readily transformed into

$$V = V_0 + \frac{1}{\sqrt{(\pi)}} \int_0^{\infty} \{e^{-(q-\lambda)^2} - e^{-(q+\lambda)^2}\} f(2qht^{\frac{1}{2}}) dq, \quad (4)$$

where  $\lambda$  has been written for  $x/2ht^{\frac{1}{2}}$ . This is the solution of the most general problem of the class considered.

In the problem of the cooling of the earth a good representation of the known data is given\* by assuming  $P = Ae^{-ax}$ , where  $A$  and  $a$  are constants. Then  $V_0$  is  $\frac{A}{a^2k}(1-e^{-ax})$ . The initial temperature at any point would be the melting point of the rocks at that depth under the pressure there. This may be taken to be of the form  $S+mx$ . Then

$$f(x) = S+mx - (A/a^2k)(1-e^{-ax}) \quad (5)$$

and the problem can be solved. We find†

$$V = (A/a^2k)(1-e^{-ax}) + mx + (S-A/a^2k) \text{Erf } \lambda \\ + (A/2a^2k) e^{\gamma^2} [e^{-ax} \{1 - \text{Erf } (\gamma - \lambda)\} - e^{ax} \{1 - \text{Erf } (\gamma + \lambda)\}] \quad (6)$$

where

$$\gamma = aht^{\frac{1}{2}}, \quad (7)$$

and

$$\lambda = x/2ht^{\frac{1}{2}}. \quad (8)$$

We shall assume that at the present time the second line is small in comparison with the first. Differentiating with regard to  $x$ , and then putting  $x$  equal to zero, we find that the rate of increase of temperature with depth at the surface is given by

$$\left(\frac{\partial V}{\partial x}\right)_0 = m + \frac{S}{h\sqrt{(\pi t)}} + \frac{A}{ak} \left(1 - \frac{1}{ah\sqrt{(\pi t)}}\right). \quad (9)$$

Let us now consider the cooling of a continental region. The average value of  $\left(\frac{\partial V}{\partial x}\right)_0$ , as determined by borings, is about  $0.00032^\circ$  C. per centimetre. Following Holmes, I shall take  $m$  to be  $0.00005^\circ$  C. per centimetre.  $S$  is the melting point of average continental rocks. This is somewhat uncertain, since it is affected by the presence of water. It will be assumed to be  $1200^\circ$  C. In the absence of water this would probably be about correct for granitic rocks; it would be higher for the basaltic rocks that occur at a small depth, but water would reduce it, so that this value may not be far wrong on the whole. The conductivity  $k$  is about  $0.005$  C.G.S. for average rocks;

$$\rho = 2.8 \text{ g/cm}^3, \quad (10)$$

$$\sigma = 0.25 \text{ cal/g. } 1^\circ \text{ C.} \quad (11)$$

Then

$$h = 0.084. \quad (12)$$

The age of the earth since solidification, denoted by  $t$ , we may take to be  $1.6 \times 10^9$  years or  $5.0 \times 10^{16}$  sec. in accordance with Holmes's results, based on

\* Holmes (*loc. cit.*).

† This solution has previously been obtained by L. R. Ingersoll and O. J. Zobel, 'Mathematical Theory of Heat Conduction,' Ginn and Co., 1913.



the uranium-lead ratio.  $A$  is  $1.03 \times 10^{-12}$  cal./cm.<sup>3</sup> sec.\* Then in equation (9) all the quantities are known except  $a$ , for which we may therefore solve. We find

$$a = 6.5 \times 10^{-7} / \text{cm.} \quad (13)$$

Thus at a depth of 15.3 km. the rate of production of heat by radioactivity should be  $e^{-1}$  of that at the surface. The ratio of the rates of production of heat by basic and acidic rocks is about 0.29, so that if the rocks at a depth of 10 km. are predominantly basic this result will be reasonable. On geological grounds this appears acceptable. It may be noticed that the value of  $a$  found by Holmes was  $4.0 \times 10^{-7} / \text{cm.}$ ; the difference is chiefly due to his having, by means of a special assumption about sub-oceanic conditions, attempted to deal with average rocks, whereas the data adopted here definitely refer to the continental areas.

We may observe that with the numerical values now obtained,

$$\gamma = 12,$$

approximately; unless  $x$  is greater than 2000 km.,  $\gamma - \lambda$  will be greater than 3, and it will be justifiable to approximate to the error functions according to the formula

$$1 - \text{Erf } \theta = \frac{e^{-\theta^2}}{\theta \sqrt{(\pi)}}. \quad (14)$$

The equation (6) now simplifies to

$$V = mx + \left( S - \frac{A}{a^2 k} \right) \text{Erf } \lambda + \frac{A}{a^2 k} (1 - e^{-ax}) + \frac{A \lambda e^{-\lambda^2}}{a^2 k \sqrt{(\pi)} (\gamma^2 - \lambda^2)}. \quad (15)$$

The last term is at most of order  $1/\gamma^2$  of the third, and with the values adopted this ratio is about 0.01. Thus the last term is small compared with the second and third, and the assumption that it is negligible is justified.

The thermal data available for the rocks below the ocean are still more scanty than those for continental rocks, owing to the fact that no deep oceanic boring has yet been made. The value of such a boring in guiding research in this subject could hardly be exaggerated. There is, however, some reason to believe that the surface rocks of the oceans are predominantly basic. It will be assumed here that they have a content of radioactive matter equal to that of basic igneous rocks within the continents, giving a rate of heat production of  $0.29 \times 12^{-12}$  cal./cm.<sup>3</sup> sec. The rate of evolution of heat will be supposed to decrease with depth according to the same law as within the continents. With these assumptions the problem of the cooling of the sub-oceanic regions is determinate.

\* Holmes, 'Geological Magazine,' February, 1915, pp. 60-71.

2. *The Compression Available for Mountain Building.*

In my former paper I considered the effect of thermal contraction in a spherical earth in producing crumpling of the surface rocks. The formula found was based on an expression for the temperature agreeing with (15) except that the last term was omitted. The error had not then been evaluated, but has now been proved unimportant. The compression was found to be given by

$$K = \frac{6\beta h}{c} \left(\frac{t}{\pi}\right)^{\frac{3}{2}} \{\epsilon + \epsilon' \alpha + \epsilon' m h \sqrt{(\pi t)} + \epsilon' \beta \sqrt{(2)}\}, \quad (16)$$

where  $K$  is the fraction of its length by which any great circle has been shortened by compression ;

$$\alpha = A/a^2k \quad \beta = S - \alpha, \quad (17)$$

$c$  is the radius of the earth ;

the coefficient of linear expansion of the rocks is  $\epsilon + \epsilon' V$ , where  $\epsilon$  and  $\epsilon'$  are constants.

We have  $c = 6.4 \times 10^8$  cm. (18)

$$\epsilon = 7 \times 10^{-6} \div 1^\circ \text{ C.}, \quad (19)$$

$$\epsilon' = 2.4 \times 10^{-8} \div (1^\circ \text{ C.})^2, \quad (20)$$

following Fizeau.

For continental regions we have

$$\alpha = 490^\circ; \quad \beta = 710^\circ, \quad \text{and hence} \quad K = 3.7 \times 10^{-3}. \quad (21)$$

For oceanic regions,

$$\alpha = 139^\circ; \quad \beta = 1061^\circ, \quad \text{and} \quad K = 5.2 \times 10^{-3}. \quad (22)$$

The area of the land surface of the earth is  $1.45 \times 10^{18}$  cm.<sup>2</sup>, and that of the ocean surface is  $3.67 \times 10^{18}$  cm.<sup>2</sup>. Hence, remembering that the proportional reduction of an area is double that of a length, we find that the reduction of the earth's surface by crumpling is  $49 \times 10^{15}$  cm.<sup>2</sup>, of which  $11 \times 10^{15}$  cm.<sup>2</sup> comes from the land and the rest from the sea. The average reduction in length of a great circle of the earth by compression is found to be 170 km.

In my previous paper the areal compression needed to account for all the existing mountains was estimated to be  $19 \times 10^{15}$  cm.<sup>2</sup>, so that the amount available appears to be two and a half times that required. The surplus, however, is not so great as this. It might be thought that oceanic crumpling should not be included at all, since it would give rise to mountains on the sea-bottom, and not to the observed continental mountains. This is, however, only partly true. On the present hypothesis the lower radioactivity of sub-oceanic rocks has enabled them to cool to a greater extent than sub-continental rocks. In addition, it appears that basic rocks are on the whole stronger than acidic ones; thus basalt has, under ordinary conditions, a crushing strength of

$12 \times 10^8$  dynes per square centimetre, as against  $8 \times 10^8$  dynes per square centimetre for granite.\* On both grounds, therefore, the rocks below the oceans must be stronger than those below the continents. Now, where the compressed ocean floor abuts on a compressed continent, the weaker will be the first to give way; the ocean floor will be partly forced over the continent, and the marginal rocks of the continent will be driven inwards and piled up over those already there. This will produce ranges of mountains nearly parallel to the coast, with much overthrusting, which correspond to the Pacific type of mountain range, such as the Rockies and the Andes. Such mountains are evidently, if this theory is correct, formed by the relief of sub-oceanic and not sub-continental compression, so that in these cases the compression produced has been derived from the oceanic rocks. It is not possible to state how much of the compression needed to form other mountains has been provided in a similar way, but the amount may be considerable. We may therefore say that the compression available on the thermal contraction theory is probably enough to account for all the existing mountains of the globe.

It may be pointed out that if the age of the earth since solidification was only  $1.6 \times 10^7$  years, which is about that determined from the cooling of the sun if no unknown source of energy is available,  $S/h\sqrt{(\pi t)}$  is  $0.00036^\circ \text{C. per centimetre}$ . Thus, at the present time, even without any primitive increase of temperature inwards, and without any supply of heat from radioactive sources, the rate of conduction of heat from the earth would exceed the actual rate. This presents a difficulty to this theory, and is avoided by the acceptance of the greater age of the earth.

[*Note added May 30, 1921.*—It is often stated as an objection to the thermal contraction theory of mountain building that the gradual cooling would give rise to mountains in all geological ages, whereas it is known that there have been long intervals of quiescence. When the strength of the earth's crust is taken into account, however, these intervals of quiescence become a natural consequence of the theory. It appears that the stress-difference produced in the crust by the cooling of the interior increases only gradually, and it is not until it reaches the crushing strength of the rocks that yield takes place and mountain building follows. A local failure of strength will rapidly spread and the formation of mountains will continue until the stresses are almost completely relieved. Thus the fact that all the great mountain chains were elevated in Tertiary times is readily accounted for.

In the case of Palæozoic and pre-Palæozoic mountains, many possible

\* Landolt and Börnstein, 'Physikalische Tabelle.'

causes of uplift can be suggested, as Dr. J. W. Evans has pointed out. If tidal friction for the last 1000 million years has been as potent as now (and it is more likely to have been more potent than less), the earth would at the beginning of that interval have rotated twice as fast as now, and the corresponding change of ellipticity must have been of great importance in mountain building.]

### 3. *The Compensation of Crustal Inequalities.*

The arguments concerning the existence of some horizontal variation of density within the crust of the earth, which partially neutralises the disturbances of surface gravity caused by the irregular form of the land surface, are partly geodetic and partly physical; but the latter have scarcely been adequately discussed. It was observed by Bouguer in Peru that the attraction of a mountain there was much less than would be expected from its size, and Laplace inferred from this that the matter composing it was lighter than the average. Pratt made a similar discovery about the Himalayas, and from his work the modern developments of the theory have sprung. The essential feature of the theory of isostasy is that the matter below mountains is supposed to be lighter than the average, while that below seas is, on the whole, denser. The amount of the excess or deficiency is just enough to balance the attraction of the surface inequalities on a particle a considerable distance away. It follows that, if an equipotential surface be taken below these inequalities, and columns of the same cross-section bored down to it from the surface, the masses in all of them are equal. This may be expressed more precisely by saying that the geoid has the form of the outer surface of a fluid earth, with the same radial density-distribution and speed of rotation as the actual earth. Now we come to the physical aspect of the problem. This result would hold if the pressure all over the standard equipotential were nearly uniform, and the interior of the earth nearly free from shearing stress. This condition indicates that, within the standard equipotential, the stress across any plane is probably perpendicular to that plane; in other words, the interior is in a hydrostatic state.

There are two alternative reasons why this hydrostatic state should exist. It may be primitive; that is to say, the inequalities may have been compensated from the earliest times. The question of its origin will then be bound up with that of the inequalities themselves. Though this may be true of part of the compensation, it is certainly not true in every case of compensation. For though it is usually held that the great continents and oceans have, on the whole, kept very much the same positions throughout

geological time, it is quite certain that there have been very great changes in level in detail; in particular, cases of rising and sinking of the coast are well known, and the elevation of mountain ranges must have produced huge stresses. It is concerning these very features that the geodetic evidence for the existence of some sort of compensation is clearest, as may be seen from the results of the United States Geodetic Survey and the Indian Survey. There must therefore be some agency that tends towards the readjustment of departures from the hydrostatic state, possibly coarsely and intermittently, but yet ensuring that no departure exceeding a certain amount, in the United States apparently about 200 metres, can persist for a long time. It may even be that many surface inequalities are compensated from the time they are formed. The nature of this readjustment requires some consideration. The assumption of Hayford and other American geodesists is that, below any mountain, the density is below the average by an amount proportional to the height of the mountain, this reduction extending to a uniform depth of 96 km., according to the latest calculations of William Bowie.\* In previous investigations, it was found that the assumption that the defect of density is the same at all depths down to this level of compensation, makes little difference to the accuracy with which the solution obtainable represents the observed gravity anomalies. Now it is obvious that if a mountain were the result of addition of matter to, or a denudation valley the result of removal of matter from, the outer layers of the earth, any compensation produced by expansion or contraction below must arise from displacements taking place both horizontally as well as vertically. For, if there is no horizontal motion, the mass in a vertical column must remain the same, and there can therefore be no compensation. Thus horizontal displacement is essential to the production of compensation.

Again, the nature of the compensation must not violate the known properties of matter. Ordinary matter does not decrease in density when a pressure is applied to it, as is supposed to happen in this case when the mountain is superposed. The requisite reduction in mass cannot therefore be caused by the mere mechanical effects of pressure on a single substance; if it is an effect of pressure at all, it must consist in the partial replacement of a dense substance by a light one, or *vice versa*. Accordingly, the mechanism of the adjustment must be, in the case of the mountain, that heavy matter flows out horizontally from below, while a certain amount of lighter matter may enter in the upper layers, though there is no clear evidence on this point. The matter near the bounding surface between the

\* 'Investigations of Gravity and Isostasy,' Spec. Pub. No. 40, U.S. Coast and Geodetic Survey, 1917.

light and heavy materials must sink downwards to some extent, so as to continue to fit the zone whence the heavy matter has flowed; but, as the rocks of which the mountain is composed are lighter than those below, compensation will be reached when the volume of the rocks displaced is less than that of the mountain, so that the mountain will remain as a projection on the surface even when the process is complete. In the same way, the removal of matter by denudation and its re-deposition elsewhere give rise to inequalities, which will in time come to be compensated. The flow must evidently take place below the layer of compensation, as was pointed out by Barrell;\* for the layer in which it occurs must be in a hydrostatic state, and therefore can transmit no shearing stress; on the other hand, any horizontal displacement can only be produced by shearing stress; and hence a surface inequality can never cause a horizontal displacement on the opposite side of a layer that is by hypothesis unable to transmit shearing stress. Hayford's hypothesis, however, demands that an inequality shall cause a displacement as far down as the level of compensation; it follows that the flow must take place below, and probably a long way below, the layer of compensation.

Suppose then that the density of the matter constituting the mountain is  $\sigma$ , and that the mean elevation of its surface over the mean surface of the land would, in the absence of compensation, be  $h$ . Let the density of the matter at the level of the flow be  $\rho_0$ . Then compensation will be attained if the thickness of the latter is diminished by  $\sigma h / \rho_0$ . The region above this will sink by approximately this distance throughout. Now if the initial density at distance  $r$  from the centre was  $\rho$ , this shows that the density at the same distance afterwards is equal to the original density at distance  $r + \sigma h / \rho_0$  from the centre, or  $\rho + \frac{\sigma h}{\rho_0} \frac{d\rho}{dr}$ . The density diminishes towards the surface, so that

the change in density owing to the compensation, being  $\frac{\sigma h}{\rho_0} \frac{d\rho}{dr}$ , is negative.

This is a constant if  $\rho$  is a linear function of  $r$ . Accordingly, Hayford's hypothesis that the defect of density is the same at all levels is true if the density under plains increases uniformly with depth until we reach the layer of compensation, below which it remains constant as far down as the layer of flow. There is nothing inherently improbable about this, and it is clear that the charges of artificiality often made against Hayford's hypothesis are unfounded. If there is a sudden change in density at any level, the compensation must be concentrated in that level. There is some evidence, from the behaviour of earthquake waves, that there is a discontinuity of substance at a depth of about 30 km., while the density must

\* 'Journal of Geology,' 1915-16.

increase gradually with depth on account of the increasing percentage of heavy constituents. Thus the true distribution of compensation is probably intermediate between these two extreme hypotheses.

It must be noticed, however, that the American observations deal almost wholly with the compensation of differences of level within a continent. The smallness of the residuals given by Hayford's Solution C,\* in which the sea was supposed compensated according to Helmert's hypothesis and the land uncompensated, in comparison with the Bouguer solution, in which both were supposed uncompensated, shows that the general features of the ocean are probably compensated, at least within some distance of the order of 2000 km. of the coast. It affords no reason for believing that even the major inequalities are compensated at greater distances from land than this, and none for believing that inequalities of small horizontal extent are compensated even within the region for which it really provides information.

Accordingly, the problem of the compensation of the oceans cannot be regarded as solved. Two important questions remain: first, whether the oceanic regions as a whole are associated with rocks of higher density; and second, whether regions of specially great or small depth in the oceans, with horizontal dimensions small compared with the oceans as a whole, are associated with especially large or small quantities of dense rock so as to compensate for their departures from the mean depth. The first question will be referred to as that of the general compensation of the oceans, and the second as that of the local compensation of the oceans. In the following sections I propose to deal with certain physical arguments that appear to throw light upon these matters, pending a decision from the determination of gravity at sea, and to develop further consequences of the same theory.

#### 4. *The General Compensation of the Oceans.*

Apart from the ellipticity of the earth due to rotation, which is practically the same for land and sea, so that there is no inequality in this case sufficiently important for the question of its compensation to arise, the chief departure of the earth from the spherical form is represented by the first harmonic. This expresses the existence of the land and water hemispheres, the former of which includes nearly all the land of the earth. It is not difficult to see that any first harmonic in the difference of elevation between the lithosphere and the geoid must be compensated. In a homogeneous earth such a first harmonic inequality could not exist. For it would be equivalent to a mere bodily displacement, the earth remaining a perfect spheroid. Hence the equipotential surfaces would be displaced by the same

\* 'The Figure of the Earth and Isostasy,' 1909, p. 169.

amount, so that their centre would again be at the new position of the centre of the earth. Thus the geoid and the lithosphere would be concentric, and the average depth of the ocean in any hemisphere would be the same.

When heterogeneity of density is taken into account a peculiar result is obtained. It is well known that the potential due to a gravitating body at a distant point is of the form

$$f(M/r + \text{solid harmonics of the second and higher orders}), \quad (23)$$

where  $f$  is the constant of gravitation,  $M$  the total mass, and  $r$  the distance of the point from the centre of mass of the body. In the case of bodies differing only slightly from the spherical form, this formula is known to be accurate to the first order of magnitude right up to the surface. Since for purely first harmonic deformations no harmonics of higher order than the first can arise, the equipotentials right up to the surface are spheres whose centre is the centre of mass of the body. In other words, whatever first harmonic deformations may exist, they produce equal displacements of the centre of mass of the whole and of the equipotentials near the surface. Thus, whatever may be the physical conditions that may give rise to a first harmonic deformation, it is necessarily completely compensated, merely as a consequence of the law of gravitation itself. No information about the nature of isostasy, therefore, can be obtained by considering the inequality that gives rise to the land and water hemispheres; it would be compensated even if the earth were a perfectly rigid body. One observable consequence of this must be that gravity far from shore in the Pacific Ocean cannot show a systematic difference from its values at geoid level in the continents.

At the same time, no light can be thrown on the general question of the compensation of the oceans by considering the land and water hemispheres; it must be approached either by means of special information or from physical considerations about the earth's interior. Barrell considered that the American and other observations he discussed agreed best with the supposition that the layers in which isostatic flow takes place, which he called the asthenosphere, are at a depth of the order of 300 km. This estimate agrees significantly with what would be expected on the theory of a cooling earth. We may legitimately suppose that at least the siliceous part of the earth, extending to a depth of the order of 1200 km., was fluid when solidification was taking place at the surface or near it. The melting point in the interior would of course be much raised by pressure, but it appears likely that the convective agitation that must have taken place during solidification, owing to the sinking and re-melting of surface fragments, would ensure that a very great



depth of rock solidified at about the same time. Since then, however, the interior has scarcely cooled at all, and must therefore still be in very nearly the same condition as immediately after solidification. We should, therefore, expect it to be extremely ready to flow under small shearing stress lasting for a considerable time. The fact that earthquake waves can be transmitted through it does not affect this argument, since the stresses involved in them continue for only a few seconds. Cooling near the surface, on the other hand, has very much increased the strength there. Thus we should expect that the depth where strength becomes low should be of the same order of magnitude as the depth at which cooling is just becoming important. This can be seen from (15) to be of the order of  $2ht^{\frac{1}{2}}$  or 370 km., in good agreement with Barrell's estimate, again on the hypothesis of the longer age of the earth.

This estimate of  $2ht^{\frac{1}{2}}$  is equally applicable to continental and oceanic regions, and consequently we may infer that any inequality capable of producing appreciable shearing stresses at a depth of about 400 km. must cause flow. Thus any inequality of height more than 200 m. and extent more than 1000 km. should be compensated. The general compensation of the oceans may therefore be inferred from the theory.

The local compensation of the oceans is on a somewhat different footing. At depths of the order of 200 km. the cooling has been greater under the oceans than under the continents, and accordingly it is likely that the size of the uncompensated inequalities needed to cause flow there is greater than that indicated by Hayford's work for similar inequalities in the United States. Thus larger uncompensated inequalities, of extent comparable with 600 km., may be expected to exist. These would produce maximum stress-differences at depths of about 200 km., and at greater depths the stress-differences would rapidly decline, so that their existence would be compatible with the much lower strength of the zone below.

### 5. *On the Origin of Oceanic Deep.*

In consequence of the greater cooling of the rocks at depths of 100 to 200 km. below the oceans, these must have tended to contract more than rocks at equal depths below the continents. The surface, however, must have remained at almost constant temperature on account of the cold water at the sea bottom. This would give rise to a phenomenon comparable with the bending of the covers of a book when held in front of a fire. The contraction of the side next the fire is due to loss of moisture, in the latter case, and to fall of temperature in the former. The margins of the sub-oceanic crust must tend to curl towards the contracting side; thus the ocean floor must

tend to sink near the coasts and to rise in the middle. This will produce an additional downward pressure near the margins and a reduced one in the middle, which must cause a stress-difference in the asthenosphere. This will therefore yield so as to permit such a crust movement to take place.

At a depth of the order of 100 km. oceanic rocks have cooled about  $300^{\circ}$  more than continental ones. Young's modulus for materials at this depth is known from earthquake data to be about  $15 \times 10^9$  dynes/cm.<sup>2</sup>, and hence the tension needed to prevent the crust from curling must be about  $3 \times 10^9$  dynes/cm.<sup>2</sup>, with the coefficient of linear expansion already adopted. This is a very large amount. The crushing strength of basalt, which is probably typical of these deep rocks, is  $1.2 \times 10^9$  dynes/cm.<sup>2</sup>. It must be remembered, however, that the pressure is very great, while the temperature is on an average several hundred degrees below the melting point. In these circumstances it is known from experiment that the strengths of rocks are many times greater than under atmospheric pressure. It is therefore probable that the rocks could endure this stress-difference without yielding, even if the ends were held tight so as to prevent the curvature needed to readjust it.

The determination of a complete formal solution of the problem of the straining of a portion of the earth's crust by cooling would be very laborious. As only an estimate of the order of magnitude of the possible deformation is required, we shall, therefore, discuss only the following related problem for the cylindrical case.

A fluid is in equilibrium in the form of an infinite circular cylinder, the force of gravity at the surface being normal to the axis. On its surface an infinite strip of solid matter floats, its curvature being equal to that of the surface of the fluid. It then contracts by cooling, the relative contraction that would be produced at any depth,  $x$ , in the absence of stress, being  $\alpha$ . The solid is supposed to have Young's modulus  $E$ , and Poisson's ratio zero. It is assumed that after contraction it remains a portion of a cylinder. Find the elevation of the centre above the margins.

Let  $2R$  be the width of the strip,  $c$  the radius of the cylinder, and  $c_1$  that of the nearest cylindrical strip after the cooling. Let the elevation of any point of the surface above the undisturbed position be  $\zeta$ , and the difference between the values of  $\zeta$  at the centre and at the margins,  $H$ . Then the original length of the arc at depth  $x$  was  $2R \left(1 - \frac{x}{c}\right)$ , and the natural length after cooling is  $2R \left(1 - \frac{x}{c} - \alpha\right)$ . The actual length is  $2R \left(1 - \frac{x}{c_1}\right)$ . Hence the amount of stretching is  $2R \left(\frac{x}{c} + \alpha - \frac{x}{c_1}\right)$ , and the tension is  $E \left(\frac{x}{c} + \alpha - \frac{x}{c_1}\right)$ . The

strain energy is therefore  $ER \int \left( \frac{x}{c} - \frac{x}{c_1} + \alpha \right)^2 dx$  taken through the strip. The gravitational energy is  $\int \frac{1}{2} g \rho \zeta^2 dy$ , where  $y$  is the element of arc of a section of the cylinder, and the integral is taken across the strip. The approximate solution desired will be obtained by making the total energy a minimum.

Remembering that the mean value of  $\zeta$  must be zero, from the condition that the strip is still floating, we see that

$$\zeta = \left( \frac{1}{3} - \frac{y^2}{R^2} \right) H. \quad (24)$$

We also notice that

$$c_1 \left( 1 - \cos \frac{R}{c_1} \right) = c \left( 1 - \cos \frac{R}{c} \right) + H. \quad (25)$$

If powers of  $R$  above the second be omitted, this gives

$$1/c_1 - 1/c = 2H/R^2. \quad (26)$$

The energy reduces to

$$\frac{4}{45} g \rho H^2 R + ER \int \left( \alpha - \frac{2Hx}{R^2} \right)^2 dx. \quad (27)$$

The equilibrium condition is obtained by differentiating this with regard to  $H$ . Hence

$$\frac{8}{45} g \rho H - E \int \frac{4x}{R^2} \left( \alpha - \frac{2Hx}{R^2} \right) dx = 0. \quad (28)$$

With  $g = 981 \text{ cm./sec.}^2$ ,

$$\alpha = 4 \times 10^{-3}, \quad x = 100 \text{ km.}, \quad R = 2000 \text{ km.}$$

we see that the first term is of the order of sixty times that under the integral sign involving  $H$ . In other words, the tendency to curve is mostly balanced by the disturbance of hydrostatic pressure, so that the curvature that actually takes place is only a small fraction of what would occur in the absence of gravity. With the above values of the quantities involved,  $H$  is found to be nearly 1 km. Thus, we should expect to find that the chief oceans will have regions around their margins deeper, by a distance of the order of a kilometre, than the centres.

This bears a suggestive resemblance to the facts with regard to oceanic deeps. All the chief deeps in the Pacific are near the margin: there are depths of 8500 m. near the Kurile Islands, 6000 m. off the Aleutian Islands, 7600 m. off Chile, 9000 m. near the Marianne Islands, and a strip of depth 9000 m. to the north of New Zealand. The last two are now in mid-ocean, but are near the edge of a former continent. The mean depth of the oceans is about 5000 m., so that some of these regions are too deep to be altogether accounted for in this way unless the difference of cooling is supposed to

extend to a greater depth than 100 km. : but this, of course, is quite probable. The same is true on a smaller scale in the Indian Ocean. Off the coasts of Australia, Java and Sumatra there are depths of 6000 m., while the middle is occupied by a huge area whose depth does not exceed 4000 m. In the Atlantic, again, shallow strips extend from the south up the middle, past S. Georgia, Tristan d'Acunha, St. Helena, and Ascension, and from the north right down the centre to the Azores. Thus, each ocean has a region of smaller depth in the middle, as is predicted by the theory.

A possible test of this theory is afforded by the fact that the inflow of matter from the margins towards the centre required by the theory is not caused by any additional weight on the surface. Thus, it corresponds to a net transference of mass towards a particular region. The mass per unit area at a deep should therefore be less than that at the centre of the ocean. Hence this should be indicated by a true defect of gravity at sea-level in the deeps ; in a gravity determination it should therefore appear as if the deeps were uncompensated. The evidence at present available on this point is meagre. Duffield's observations\* on the "Morea" indicate a defect of gravity over the deep parts of the Indian Ocean of about the theoretical amount, but are open to some uncertainty. Nevertheless it would be a remarkable coincidence if accidental errors have happened to produce low values of gravity at all the places where they should theoretically have been expected, and so far as the observations go they definitely support the theory.

The gravity anomalies here predicted do not arise from a permanent strength in the asthenosphere, which is on this theory in a hydrostatic state, as under a mountain chain ; they arise from the strength and tendency to curvature of the strong upper crust. Faulting may occur near the margins. A reversed effect may be looked for in the continents, but is probably masked by denudation and sedimentary rocks.

#### 6. *The Formation of Geosynclines.*

It has been seen that the addition of a thickness  $h$  of matter of density  $\sigma$  depresses the crust by an amount  $\sigma h / \rho_0$ , so that the upper surface of the new matter is  $\left(1 - \frac{\sigma}{\rho_0}\right) h$  above the original surface. If the deposition takes place from water, the additional mass is only the excess of the mass of the sediments over that of the water displaced. Let  $\rho_1$  be the density of the sediments and  $\rho_2$  that of the water,  $h$  the depth of sediment deposited, and  $x$  the depression of the original surface. Then the mass per unit area is

\* "On the Determination of Gravity at Sea," 'Brit. Assoc. Report, Newcastle,' 1916, pp. 549-565.

increased by  $\rho_1 h - (h-x)\rho_2 - \rho_0 x$ , and the condition for compensation is that this shall vanish. We find that

$$(h-x)/h = (\rho_0 - \rho_1)/(\rho_0 - \rho_2). \quad (29)$$

But  $h-x$  is the reduction in the depth of the water. We therefore see that the depth of sediment that can be deposited in a sea whose initial depth is known is a determinate multiple of this depth. If we take  $\rho_0$  to be 3.2, which is probably typical of the rocks at a depth of some hundreds of kilometres,  $\rho_1$  to be 2.2, and  $\rho_2$  to be 1.0, it is seen that the maximum depth of the sediments is 2.2 times the original depth of the water.

The possibility of deposition of sediments to a depth far greater than the initial depth of the water in which they are formed is obviously of considerable geological importance; but the depression of the sea bottom that can be produced in this way has been much exaggerated, as has been pointed out by A. Morley Davies.\* If the stress differences present become too small to cause flow, compensation will not proceed. Accordingly, the adjustment that takes place can never be greater, and may be less, than the amount needed to give compensation. But very many cases are known where the existing deposits are far more than 2.2 times as deep as the sea can have been when their formation commenced, and for these the theory of isostatic compensation is therefore inadequate. To account for them we must have a theory that will explain how the crust in a region of deposition can be depressed by an amount far in excess of that needed to give compensation. Again, some of these sedimented regions afterwards rise far above sea-level, implying a flow of matter into them for which there could be no explanation if the depression of the crust at the end of the sedimentation was less than or equal to the amount needed to neutralise the effect of the weight of the sediments. Accordingly, there must be important departure from isostasy at certain stages of the development of such regions, and no explanation of the existence of sedimental rocks above sea-level can be satisfactory unless it takes them into account.

A method by which these extensive sedimented regions can afterwards be uplifted is suggested by the theory of the origin of deeps just described. The sediments from a continent must often be deposited in a gradually developing deep. Their weight will accentuate the tendency already existing for that region to sink. Hence the stresses in the crust will be increased, and may lead to fracture. When this takes place, the crust on the oceanward side will be free to bend down further. That on the landward side of the fault, however, will now have nothing to hold it down

\* 'Geological Magazine,' 1918, pp. 125 and 233; E. M. Anderson, *loc. cit.*, p. 192.

except the weight of the sediments. Accordingly, it will be free to rise above sea-level. If compression occurs afterwards, a greater thickness of light sedimentary rocks is accumulated, and hence the surface will be raised still higher.

*7. The Stresses in an Elastic Solid due to Changes of Temperature.*

In the present discussion the earth will be replaced by an elastic sphere of variable elasticity and density, and the changes of temperature considered will always be symmetrical about the centre and confined to the neighbourhood of the surface. The errors arising from the neglect of the ellipticity of the earth are very small.

Let the excess of temperature at any point  $(x, y, z)$  over the initial temperature there be  $V$ ;  $(u, v, w)$  the component displacements of the matter originally there;  $n$  the coefficient of linear expansion;  $\lambda$  and  $\mu$  the elastic coefficients of the matter there; and  $P, Q, R, S, T, U$  the six stress-components.

Then the equations of equilibrium are three of the form

$$\frac{\partial P}{\partial x} + \frac{\partial U}{\partial y} + \frac{\partial T}{\partial z} + \rho X = 0, \quad (30)$$

where  $\rho$  is the density and  $(X, Y, Z)$  the bodily force per unit mass. Now consider how the stresses  $P, Q, R, S, T, U$  can arise. Before the change of temperature they had the values  $P_0, Q_0, R_0, S_0, T_0, U_0$ , say. When an element moves from  $x, y, z$  to  $x+u, y+v, z+w$ , it retains its original stress, to which is added the new part, namely, the stress needed to produce the changes of the element in size and shape, from the form it would have had if it simply expanded without strain, to the form it actually takes. The alterations in dimensions due to simple expansion in the absence of stress would make

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} = \frac{\partial w}{\partial z} = nV; \quad \frac{\partial u}{\partial y} = \frac{\partial u}{\partial z} = \frac{\partial v}{\partial x} = \frac{\partial v}{\partial z} = \frac{\partial w}{\partial x} = \frac{\partial w}{\partial y} = 0. \quad (31)$$

Now the six components of stress depend on the changes of the quantities

$$\frac{\partial u}{\partial x}, \frac{\partial v}{\partial y}, \frac{\partial w}{\partial z}, \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}, \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}, \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}, \quad (32)$$

from their amounts corresponding to simple expansion to their final amounts. Thus, in the stress-strain relations of the ordinary theory of the deformation of an elastic solid we must put the first three of the strains equal to  $\frac{\partial u}{\partial x} - nV, \frac{\partial v}{\partial y} - nV, \frac{\partial w}{\partial z} - nV$ , while the other three are of the form  $\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}$

as in isothermal straining. If the extra stresses be denoted by  $P_1$ , etc., their values are therefore given by

$$P_1 = \lambda\delta + 2\mu \frac{\partial u}{\partial x} - (3\lambda + 2\mu)nV, \text{ with two symmetrical relations; } (33)$$

$$S_1 = \mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \text{ with two symmetrical relations; where } (34)$$

$$\delta = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}. \quad (35)$$

The bodily forces  $X, Y, Z$  can also be regarded as composed of two parts, namely,  $X_0, Y_0, Z_0$ , the forces at  $x, y, z$  before the deformation, and  $X_1, Y_1, Z_1$ , the additional forces acting on the same particle caused by the deformation. The equations of strain are then three, of the form

$$\begin{aligned} \frac{\partial P_0}{\partial x} + \frac{\partial U_0}{\partial y} + \frac{\partial T_0}{\partial z} + \frac{\partial}{\partial x} \left( \lambda\delta + 2\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left\{ \mu \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) \right\} + \frac{\partial}{\partial z} \left\{ \mu \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \right\} \\ - \frac{\partial}{\partial x} \{ (3\lambda + 2\mu)nV \} + \rho(X_0 + X_1) = 0. \end{aligned} \quad (36)$$

Further progress is impossible without knowledge of the initial stress. If this be assumed to be hydrostatic pressure, as would be correct in a planet which had solidified while stirred up by bodily convection currents produced by surface cooling, we have

$$S_0 = T_0 = U_0 = 0, \quad P_0 = Q_0 = R_0, \quad (37)$$

$$\frac{\partial P_0}{\partial x} + \rho_0 X_0 = 0, \text{ etc.} \quad (38)$$

We have also

$$\rho = \rho_0 - \frac{\partial}{\partial x} (\rho_0 u) - \frac{\partial}{\partial y} (\rho_0 v) - \frac{\partial}{\partial z} (\rho_0 w) = \rho_0 + \rho_1, \text{ say.} \quad (39)$$

$$\text{Put} \quad (3\lambda + 2\mu)nV = \gamma. \quad (40)$$

The equations of equilibrium therefore become

$$\begin{aligned} \frac{\partial}{\partial x} \left( \lambda\delta + 2\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left\{ \mu \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) \right\} + \frac{\partial}{\partial z} \left\{ \mu \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \right\} - \frac{\partial \gamma}{\partial x} \\ + \rho_0 X_1 + \rho_1 X_0 = 0, \end{aligned} \quad (41)$$

with two similar equations. These are perfectly general, provided the squares of the displacements can be neglected, and will still hold in a heterogeneous and non-spherical body.\*

\* Cf. Love, 'Problems of Geodynamics,' Camb. Univ. Press, 1911, pp. 89-92.

8. Application to the Earth.

Let the radial displacement at distance  $r$  from the centre be  $q$ . Then by symmetry, the origin being at the centre, we have

$$u = qx/r, \quad v = qy/r, \quad w = qz/r. \quad (42)$$

The radial force acting on unit mass is  $g$ , and is of course in general a function of  $r$ . Thus

$$X_0 = -gx/r, \text{ etc.} \quad (43)$$

The force acting on unit mass after the displacement is  $X_0 \left( \frac{r-q}{r} \right)^2$ , so that

$$X_1 = 2gqx/r^2. \quad (44)$$

Also 
$$\delta = \frac{1}{r^2} \frac{d}{dr} (r^2 q), \quad (45)$$

$$\rho_1 = -\rho_0 \delta - q \frac{d\rho_0}{dr}. \quad (46)$$

Substituting in (41), and remembering that  $\lambda$  and  $\mu$  are functions of  $r$  alone, we find that all three equations are satisfied if

$$\frac{d}{dr} \{ (\lambda + 2\mu) \delta \} - 2q \left( \frac{\mu}{r^2} + \frac{2}{r} \frac{d\mu}{dr} \right) - \frac{\partial \gamma}{\partial r} + g\rho_0 \left( \frac{2q}{r} + \delta \right) + gq \frac{d\rho_0}{dr} = 0. \quad (47)$$

If, now,  $H$  be of the order of magnitude of the depth to which cooling extends, we see that  $dq/dr$  must be of the order  $q/H$ , and therefore large compared with  $q/r$  in general. If  $c$  be the radius of the earth, we see that the first term in the last equation is of order  $\lambda q/H^2$ , the second  $\lambda q/c^2$ , the fourth  $g\rho_0 q/H$ , and the last  $g\rho_0 q/c$ . Accordingly, the fourth term is about a tenth of the first, and the others, with the exception of the third, not more than a hundredth of it. We can accordingly reduce the equation to

$$\frac{d}{dr} \{ (\lambda + 2\mu) \delta \} + g\rho_0 \delta - \frac{d\gamma}{dr} = 0. \quad (48)$$

Hence

$$(\lambda + 2\mu) \delta = \exp \left\{ - \int^r \frac{g\rho_0}{\lambda + 2\mu} dr \right\} \int^r \left[ \exp \int^r \frac{g\rho_0}{\lambda + 2\mu} dr \right] \frac{d\gamma}{dr} dr, \quad (49)$$

which becomes, if we neglect the square of  $g\rho_0 H/\lambda$ ,

$$= \gamma - \int^r \frac{g\rho_0 \gamma}{\lambda + 2\mu} dr. \quad (50)$$

The lower limit of the integral is at present left undetermined.

If the point considered be on the axis of  $x$ , the additional stresses are at once found to be given by

$$P_1 = \lambda \delta + 2\mu dq/dr - \gamma, \quad (51)$$

$$Q_1 = R_1 = \lambda \delta + 2\mu q/r - \gamma, \quad (52)$$

$$S_1 = T_1 = U_1 = 0. \quad (53)$$



Thus the principal stresses are radial and tangential, and it is at once seen from symmetry that this must be true at all points. Now, the tendency of the matter to flow or rupture is determined by the difference between the greatest and least of the principal stresses. As the initial stresses were equal in all directions, they do not affect the question. If  $P$ , the radial stress, be algebraically the greater, horizontal fracture will tend to occur; and if  $Q$  be the greater, the fractures will be vertical. Now,

$$\begin{aligned} P-Q &= 2\mu \left( \frac{dq}{dr} - \frac{q}{r} \right) = 2\mu \left( \delta - \frac{3}{r^2} \int_0^r r'^2 \delta \, dr' \right) \\ &= \frac{2\mu}{r^3} \int_0^r r'^2 \frac{d\delta}{dr'} \, dr' = \frac{2\mu}{r^3} \int_0^r \frac{r'^3}{\lambda + 2\mu} \left( \frac{d\gamma}{dr'} - \frac{g\rho_0\gamma}{\lambda + 2\mu} \right) dr'. \quad (54) \end{aligned}$$

Now let us suppose that no fracture has taken place since solidification, and consider the stress-difference acquired since then. The change of temperature at the centre is insignificant, while at all levels where it is appreciable it is negative. Accordingly,  $\gamma$  is always negative. The first part of the integral is therefore essentially negative, and as the second part is only a small correction to it, the integral as a whole must be negative. Thus the immediate effect of the cooling of the earth is to produce a strong tendency to vertical fracture at all depths.

On the other hand, suppose that the crust has by flow or fracture adjusted itself since solidification until the horizontal tension first produced has been completely relieved. Then the fall of temperature at the surface after this is zero, on the supposition that the temperature there is maintained only by the radiation from the sun, which is supposed constant. Hence  $\gamma$  is zero when  $r = 0$ , falls to a maximum negative value somewhere near the surface, and then increases again, reaching zero again at the surface. Now, near the surface not only is  $r$  greater than at great depths, but, in consequence of the recent work of Knott,\* we know that  $\lambda + 2\mu$  is least near the surface. Hence in the integral  $d\gamma/dr$  is multiplied by a larger quantity when it is positive than when it is negative. The first part of the integral is therefore positive when  $r = c$ , and of order  $c^2 H\gamma/(\lambda + 2\mu)$ . The integrand in the second part of the integral, allowing for the negative sign before it, is always positive. The second part of the integral is therefore positive and of order  $g\rho_0\gamma Hc^3/(\lambda + 2\mu)^2$ . Now  $\{\lambda + 2\mu/\rho\}^{\frac{1}{2}}$  is about 7 km.-sec., and therefore the two parts of the integral are seen to be both positive when  $r = c$ , and of the same order of magnitude. At depths comparable with the level of greatest cooling the integral is negative, as before. Hence, if there has been no variation in the surface

\* "The Propagation of Earthquake Waves through the Earth," 'Roy. Soc. Proc. Edin.,' vol. 39, pp. 157-208 (1919).

temperature since hydrostatic conditions were last attained, symmetrical cooling must necessarily lead to a horizontal compression at the surface and a tension below.

#### *9. The Effects of the Initial Tension near the Surface.*

It has just been shown that the cooling that immediately followed solidification must have produced a tremendous tension in the uppermost layers of the crust. This tension would be practically that which would be developed if a rock cooled down from near its melting point to ordinary temperatures while its ends were kept immovable. No rock could stand such a tension, and, accordingly, it must soon have been relieved in some way. The mode of relief seems fairly clear, though there has been some disagreement about it among previous writers. Its nature and effects appear to have been consistently neglected by geologists, presumably because it took place before the oldest known rocks were formed, but, nevertheless, it is likely to have played a very important part in determining the present configuration of the earth's surface; and relief of tension in modified form has probably continued to produce notable effects even up to the present day. Sir G. H. Darwin, in his investigation of the amount of mountain building to be expected on the Kelvin theory of the cooling of the earth, seems to have thought that the relief would take place by horizontal flow, the surface layers merely becoming somewhat thinner without change of length, and thereby acquiring a new unstressed state. This may be a satisfactory description of the phenomena at great depths, where the pressure is great; but at the surface a rock under tension would break at right angles to the tension just as any rope or bar does in air. Accordingly, the surface must have become honeycombed with vertical cracks. The depths of these would initially be very small and nearly equal, but the differences in depth would gradually grow. For suppose that a crack, A, is slightly deeper than a neighbouring one, B. Then further cooling below will produce a new tension, and the crust at A will have been more weakened by the deeper crack there, and therefore the crack A will commence to grow downwards sooner and more rapidly than the other. When cooling has progressed a long way down, the cracks must become very unequal in depth, and only a few of those originally formed will then be deep enough to continue their growth.

Now it must be remembered that, before solidification, the temperature was not uniform, because the melting point would be raised by pressure, and would therefore rise with the depth. Hence a crack extending downwards must be penetrating regions of higher and higher initial temperature as it

proceeds; but its internal pressure is necessarily atmospheric and practically constant. Hence, although the rocks at any depth are necessarily below their melting points at the pressure normally appropriate to that depth, as soon as they are reached by a crack, there will be a fall of pressure which may lower the melting point sufficiently to cause fusion; all that is needed is that the crack may reach a depth where the actual temperature is as high as the initial temperature at the surface. It may be easily shown from the equation (54) that this will be achieved at the depth of most rapid cooling, which is also a region of great tension, when cooling has proceeded for an interval of the order of  $10^7$  years, when the depth of the cracks would be comparable with 8 km. When this happens fusion must take place, and magma will be forced up the crack by hydrostatic pressure until the horizontal uniformity of pressure is nearly restored. Now the density of the matter there was probably not very different from that at the surface, and the semi-fluid magma may even have been lighter than the solids at the surface. Hence hydrostatic conditions would not be restored till the crack was practically full. Thus intrusions, not unlike the dykes of the present day, would be formed. Known dykes are not, of course, original examples of this process, being of much later date; all signs of these primitive dykes must have been buried beneath sediments and igneous outpourings long ago. On the moon, however, denudation and sedimentation do not exist, and there some relics may be sought. The well-known rills are not instances, being of later date, as is seen from the fact that in some cases they have broken through crater walls. The radiating streaks are much more likely to afford examples. These are narrow streaks, radiating as a rule from large craters; that they are filled up to the level of the surface is plain from the fact that they are extremely difficult to see under oblique illumination, which would not be the case if there were any difference of level that could cause a shadow to be thrown. In fact, the agreement in level is surprisingly good, considering that it can only arise from a more or less accidental numerical coincidence between the average density of the rocks down to the bottom of the crack, and the density of the rocks at the bottom when fused. The fact that the theory calls for such a coincidence does not, however, afford any argument against it, for the extreme smoothness of the surface of these streaks shows that they must have been filled with a semi-fluid at one time, and the support of this would have to be explained by some such balance whatever theory we should choose to adopt as an explanation of their origin. So far, therefore, we may hold that the theory is confirmed by the existence of these streaks on the moon. As it depends partly on the increase of pressure with depth,

which would be greater in the earth on account of the greater value of gravity, we may have some confidence in its applicability to the earth.

When the lateral ends of cracks are near together, the short length of crust between them has to support the whole of the unrelieved tension, and is therefore a particularly likely part of the crust for the next fracture to occur. Cracks will therefore tend to grow together, and thus will tend to develop into closed polygonal systems. When this takes place, a qualitatively different stage of the process commences. Each polygon is separate from the rest of the crust, and will therefore proceed to develop on its own account. Its surface has long ceased to change in temperature, but cooling continues below, so that there is a tendency to contract underneath. This would tend to close the cracks above by shortening the crust, were it not that the cracks have been closed already by the injected magma. Hence the shortening below can be achieved only by curvature of the crust. The centre of the polygon must therefore rise in the middle relative to the edges; its centre of gravity cannot rise, however, since that would imply the existence of a great additional pressure over the surface, which the weak matter just below would be unable to support. Accordingly, while the centre must rise, the boundary must sink. The matter below will offer little resistance to this depression, but rather will make way for some of it by breaking through the dykes that form the boundary. What reaches the surface will fuse, owing to the relief of pressure, and flow out so as to submerge the depressed portion. It is obvious from hydrostatics that it must rise to a level above the tops of the cracks, for a simple fracture would bring it nearly level with them, even if the margins were not bent down, and the curvature would be enough to send them far below the free surface. When the ejected matter solidified, which would not take long, a smooth surface would be formed. Here, again, we find a verification on the moon, for the large maria are extensive regions of great smoothness, and the regions between them are at higher levels. The bounding cracks would of course have been submerged below the outpour and become lost to sight for all time. What is particularly interesting about the maria, however, is that all the chief lie in a chain, forming the greater part of a circle, about 1000 miles in diameter, so that the suggested formation of a raised polygon is confirmed. The fact that they are darker than the average of the lunar surface, while the streaks are brighter, may perhaps be attributed to the different conditions of solidification inside a crack and in the open, or perhaps to the matter having come from a different depth.

The submersion of the matter around the edges of these polygons below hotter matter, far above its normal melting point, must have caused the depressed rocks there to melt again, or at least to soften. Now the density,

by hypothesis, increases with depth, and therefore the melted matter, being originally derived from a higher level in the crust, is lighter than its surroundings and tends to rise. The highest part of the polygon being the middle, on account of the curvature, the fused material would collect there. Thus the centre would become characterised by a greater depth of light matter than the edges; but if the average density down to a certain equipotential is excessively low at a place, a greater depth is required to give compensation. Hence, when the fused matter solidified again, even if the crust afterwards gave way under the tension involved, the centre would still remain elevated above the margins. Thus a permanent departure from sphericity would be produced. The region on the moon that has apparently been uplifted in this way is about 1000 miles across; a region on the earth of the same relative size would have a diameter of 3600 miles, about the width of Africa or North America. If such a process ever took place on the earth, we should therefore expect it to have led to the formation of elevated regions of similar size to our actual continents.

Before developing this hypothesis further let us consider certain further data about the moon which may be relevant. The lunar craters are the dominant physical feature of the continents, but they are almost absent from the maria. This is probably due to their having been formed before the maria; most of those that were originally present would then have been submerged in the outflowing lava and hidden, and only those of later origin would have examples in the maria. Streaks also are rare in the maria, for the same reason. It may be objected to the theory that after the outflow all tension in the crust would be relieved, and that therefore no cracks at all could be formed subsequently. The partial fusion of the surface by the hot liquid must, however, lead to the formation of a new hot solid surface, when tension could begin afresh, though with less violence than before. The origin of craters I have not attempted to account for. The rills may be analogous to rift valleys on the earth.

The origin of continents offers one of the most difficult problems in geophysics. Numerous attempts have been made to solve it, but none of the theories offered appear satisfactory. The tetrahedral theory is one of the best known; this starts with a newly solidified earth, and it is supposed that the contraction of the inner parts left the outer crust in a state in which it retained its original area, but had to collapse so as to accommodate itself to the reduced volume of the interior. The form adopted would, it was said, differ from the sphere in the direction of the regular solid with largest surface for the given volume, namely, the regular tetrahedron, and thus four continents would be formed, all at equal distances from one another. The

physical aspect of the theory has not been considered in detail. It derives some support from the fact that the actual distribution of land does bear some resemblance to a tetrahedron, though this is probably a peculiarity of the present time, and seems to have been widely departed from at some previous epochs. The fatal defect of the theory, it seems to me, is that a tetrahedral deformation does not correspond to a figure of equilibrium. It is known that for any such displacement the elevated parts must tend to come down again, since both gravity and the curvature of the elastic outer layer act so as to restore the original state. Instead of retaining the deformed figure, the earth would therefore oscillate about the spherical form till the oscillations were damped out, when symmetry would be restored. The shell, being too large for the interior, would then be unsupported and would collapse. A tetrahedral deformation cannot therefore be produced in this way; the way to render one possible is to have the continents free at their edges, so that curvature can take place in consequence of the natural cooling. The curved continent will then practically float on the heated interior, and any oscillation that may take place will merely move it up and down with the interior. Thus the process we have indicated is an essential preliminary of a tetrahedral deformation.

It has at various times been suggested that the birth of the moon may have had an important effect on the distribution of land and sea on the earth. This view must be examined with special care, because the hypothesis that the moon was formed from the earth by the disruptive action of the solar tides has acquired a moderate probability, though it cannot be regarded as demonstrated. It is known that the actual masses and motions of the earth and moon are such that if ever they formed one liquid body, this must have rotated in a period that would make the period of a free oscillation of tidal type very nearly coincident with the period of the solar semidiurnal tide at the same time. Accordingly the amplitude of this tide must have become very great, and it is certain that it must have become comparable with the diameter of the planet itself. If it ever exceeded a certain amount theoretically determinable, but not yet calculated, the planet must have broken up into two masses very like the earth and moon, and the rupture must have taken place in such a way that the subsequent development would be in the direction of the present state of the earth and moon; and there is little doubt now of the quantitative adequacy of tidal friction to produce the remainder of the changes, from then till now, in the motions of the two bodies. Such a series of agreements may be due to accidental coincidence, but the prior probability of this is small, and the theory may be accepted tentatively.

The importance of the effect of the rupture on geological history cannot

be determined till we know whether it took place before or after the commencement of solidification. The existence of a thin solid crust would not have affected the process much, as it would be very flexible; thus separation could have taken place at this stage. The crust would become broken into fragments; and the removal of a large quantity of surface matter from one side would leave a vast area with no light matter, which would, in the absence of redistribution, develop into the Pacific Ocean. This hypothesis is open to various objections, however. Though a thin solid crust would make little difference, the coincidence of periods would have been upset if the earth was not elsewhere almost wholly fluid. Now light solid fragments floating on a liquid interior, and largely confined to one side, would correspond to a first harmonic deformation, which has been shown to be unstable.\* The fragments would therefore spread out again and redistribute themselves generally over the earth, so that the theory is not available as an explanation of the Pacific Ocean.

Again, the ellipticity of the earth at this time must have been at least thirty times what it is now, and the formation of a new crust would only have taken a geologically short time. In the subsequent evolution, the equator must therefore have contracted by an amount of at least 2000 km., which would have caused the formation of mountain chains across the equator, running north and south, and far exceeding in size any known mountains. The solidification of the earth must then have occurred when the moon had attained a considerable distance, and the earth's speed of rotation had accordingly become much diminished. This is confirmed by the fact that the moon itself seems to have been largely fluid until it reached a distance of about 150,000 km. from the earth, so that this criticism is answerable. A further criticism is that even if the Pacific Ocean were accounted for in this way, a similar explanation would not be available for the asymmetry that exists on Mars; for Mars has certainly not acquired a satellite by fissure, and, even if it had, the equator would run through the middle of the ocean produced, whereas the dark regions on Mars, which are believed to be the seas, are nearly confined to the southern hemisphere. There must therefore be some alternative reason for an asymmetrical distribution of oceans.

#### *Summary.*

On the hypothesis that the earth was formerly molten, a theory of its thermal history is developed, based largely on the numerical results of

\* J. H. Jeans, "Gravitational Instability and the Figure of the Earth," 'Roy. Soc. Proc.,' A, vol. 93, pp. 413-417 (1917).

Arthur Holmes. In the main, Holmes's inferences are confirmed. It is found that the available compression is probably sufficient to account for all existing mountains, and an explanation of the Pacific type of mountain range is based on the greater cooling and consequent strength of the sub-oceanic rocks. A physical interpretation of the results of investigations of isostasy is offered, and is used in a discussion of the compensation of oceanic inequalities. It is shown that the inequality that gives rise to the land and water hemispheres is necessarily compensated, and that the oceans are also in the main probably compensated. An explanation of the fact that the great oceans have regions of smaller depth in the middle is founded on the greater cooling of sub-oceanic rocks. This theory requires that the deeper parts of the oceans should be associated with low values of gravity, which is capable of direct verification.

The stresses that would be set up in the earth's crust soon after solidification are discussed, and the results appear to agree with observations of the present state of the moon. A theory of the origin of continents is developed from this, and appears to have certain important advantages over those at present current.

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### *On the Absorption of Light by Electrically Luminescent Mercury Vapour.*

By E. P. METCALFE and B. VENKATESACHAR.

(Communicated by Prof. A. W. Porter, F.R.S. Received March 12, 1921.)

[PLATE 3.]

#### *Introductory.*

Some of the earliest experiments on the absorption of light by electrically luminous gases were carried out by Pfüger,\* who, in 1907, investigated the absorption and reversal of the hydrogen lines by luminous hydrogen. He used a condensed discharge in a three-electrode tube, in which a short constriction provided the source of radiation and the wider and longer part the absorbing column. He succeeded in reversing  $H_{\alpha}$ . This work was followed up by Landenburg and Loria,† who reversed  $H_{\alpha}$  and  $H_{\beta}$ . In the same year

\* 'Ann. der Phys.,' vol. 24, p. 515 (1907).

† See Wood's 'Physical Optics,' p. 434.



Kuch and Retschinsky\* made experiments on selective absorption in mercury vapour lamps. They found that the ratio of the intensities of the spectral lines in the light from the mercury vapour depends on the thickness of the radiating layer of vapour, the intensities of neighbouring lines tending to equalise as the layer increases in thickness, a result which would follow from a relatively greater absorption of the stronger lines. They also made photometric measurements of the illumination from two mercury lamps, one of which was placed behind the other so that the light from the first had to traverse the second. They discovered that the radiation from the combination of lamps, arranged thus, was less than the sum of the radiations from each separately. Pflüger† followed with photometric observations on the absorption of the lines 5461 Å.U., 4358 Å.U., 4047 Å.U., 5791 Å.U., and 5770 Å.U. Similar work was done by L. Grebe,‡ on 5461 Å.U. and 4358 Å.U. In all these experiments with luminous mercury vapour, the current densities (of the order of 2 ampères per square centimetre) and the power developed in the absorbing arcs were considerable.

#### *Preliminary Experiments.*

It occurred to the present writers that very faintly luminous mercury vapour might possibly exhibit more marked selective absorption than had been observed by previous experimenters. It was, therefore, thought worth while to look for a means of maintaining a mercury arc of very low current density. This was found possible in a three-electrode tube in which two arcs were formed, having a common cathode. This arrangement, which is somewhat similar to that used in "self-starting" vapour lamps, is shown in fig. 1. A strong arc is started between mercury pools K and A in the lower part of the vacuous tube; the third electrode B being a thick iron wire cemented in with sealing wax. Connections are made as shown. The apparatus having been pumped out to a very low pressure, an arc is struck between A and K, B being connected to the supply through a rheostat. When the ionised vapour from the arc AK reaches B, the second arc BK starts, taking a current whose strength depends on the resistance  $R_2$ . This current strength can be indefinitely diminished by increasing  $R_2$ . The low power arc BK can only be maintained in the presence of the strong ionising arc AK. If the pressure in the tube is sufficiently low and the current in BK is of the order of 0.1 ampère, the second arc fills the tube with a characteristic faint luminosity. In this state the vapour is found to exhibit marked selective absorption.

\* 'Ann. der Phys.,' vol. 22, p. 852 (1907).

† 'Ann. der Phys.,' vol. 26, p. 789 (1908).

‡ 'Ann. der Phys.,' vol. 36, p. 834 (1911).

Our first experiments were made with a bulb of this sort, through which was passed the light from an independent mercury vapour lamp carrying a

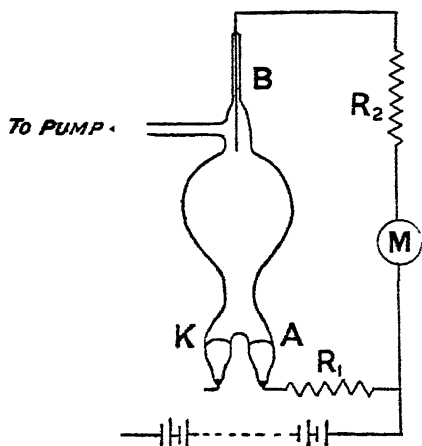


FIG. 1.

current of density about 5 ampères per square centimetres. The radiating arc was placed close to the bulb and the light traversing the bulb was focussed through a green ray filter on to a glass Fabry and Perot étalon of 5 mm. thickness. The ring system was examined while the arc BK was turned on and off. After several trials an indication of a diminution in the brightness of the rings was observed as the arc BK started. We then removed the green ray filter and placed a small piece of white paper at the focus. As the arc BK started, a very perceptible change was observed to take place in the tint of the image of the mercury lamp, the colour becoming distinctly pinkish. The effect was well marked when the current density of BK was of the order of 5 milliampères per square centimetre. It was soon found that, to produce the effect at all, it was necessary that the tube should be very completely pumped out—the more completely the better. Using the Fabry and Perot étalon, it was found possible with this tube, when the conditions were most favourable, to observe a faint dark line in the middle of each ring in the main line system.

It seemed very highly probable that the smallness of the absorption effect in these experiments was due to the shortness of the absorbing column provided by that particular shape of tube. So that our next step was to contrive a form of apparatus giving us a much longer—and also a variable length of—absorbing column.



Subsequent observations made with an échelon spectroscope showed that the unabsorbed light (*i.e.*, about 20 per cent. of the incident light) is due to the satellites of the main line in the 5461 Å.U. group, the main line itself being almost entirely absorbed. The magnitude of the absorption is very striking, considering the extreme tenuity of the vapour in the column, the lowness of the current density and the feeble luminosity of the absorbing column. We may take, as an example, an observed case where the highest temperature of the glass containing the absorbing column was about 100° C., the lowest temperature being 50° C., with a current density in the absorbing arc of about 10 milliampères per square centimetre a column of luminescent vapour 52 cm. in length absorbed 80 per cent. of the incident green radiation from the bright vapour lamp at Q.

A typical experiment with this apparatus is conducted thus. Electrical connections having been made as shown in the diagram, the tube is evacuated as thoroughly as possible with liquid-air-cooled charcoal. The arc AK is struck. The vapour from this arc rises into the horizontal part of the tube. The three-point switch, S, is connected to A<sub>1</sub>, and a voltmeter connected between A<sub>1</sub> and K shows 100 volts. An observer, looking through either of the lenses L<sub>1</sub> and L<sub>2</sub>, can see an advancing ring of condensing mercury on the sides of the tube, moving towards A<sub>1</sub>. As this ring, which marks the head of the column of ionised vapour, reaches A<sub>1</sub>, the voltage A<sub>1</sub>K gradually falls to about 60, and a discharge is seen to start, of a bright bluish-white colour. This is followed by a sudden drop in the voltage to about 20, accompanied by an equally sudden change in the colour of the discharge, as seen end-on, which becomes distinctly pinkish. It is found that the absorption produced by the bluish discharge is slight, whereas that produced by the pinkish discharge may be enormous.

A similar series of events is associated with the approach of the ionised vapour to the anodes A<sub>2</sub> and A<sub>3</sub>.

#### *Measurements of Absorption.*

With this apparatus we proceeded to measure the absorption, using a Lummer-Brodhun photometer. The light passing through the lens L<sub>2</sub> was made, by means of an additional lens, to form a uniform patch of illumination on one face of the white screen of the photometer; the other face of the screen was illuminated by a comparison mercury vapour lamp, mounted so as to slide along a 2-metre photometer bench. The position of the comparison lamp was controlled by the observer by means of a simple winch arrangement close to the photometer eyepiece. Observations were made through a green ray filter. The thermal and electrical conditions in the radiating and

comparison lamps were kept constant, as also those in the ionising arc, AK ; the current in the absorbing column was variable from zero to 0.2 ampère. Sets of typical observations are given in Tables I and II.

Table I.—Length of Absorbing Column 13 cm. Voltage Drop between  $A_1$  and K 23.5 volts.

Current density in absorbing column. Milliamps. per sq. cm.	Fraction of incident light transmitted.
3.72	0.52
5.32	0.46
6.92	0.40
7.98	0.37
9.32	0.35
10.64	0.34
11.95	0.33
13.30	0.33

Table II.—Length of Absorbing Column 35 cm. Voltage Drop between  $A_2$  and K 53 volts.

Current density in absorbing column. Milliamps. per sq. cm.	Fraction of incident light transmitted.
0.75	0.89
1.00	0.70
2.71	0.34
5.42	0.29
8.12	0.29
13.55	0.22

With the 52-cm. column the absorption is so heavy that a succession of measurements of progressive absorption is hardly possible, since the limiting value of the transmitted fraction is reached with a current density of 1 milliampère per square centimetre. The voltage drop between  $A_2$  and K in this case was 75 volts. The observations recorded in the two Tables above are plotted in fig. 3.

It must be noted that in the above experiments the radiation from the absorbing column is negligible, and the fraction of the incident light transmitted tends to a limiting value which appears to represent the ratio of the sum of the intensities of the satellites of the main line to that of the complete group constituting 5461 Å.U. The satellites are only very slightly (indeed quite imperceptibly) absorbed under the conditions of the experiment recorded in Table I (viz., low current density and shortness of absorbing

column). As will be mentioned later, one of the satellites has been observed to be absorbed under certain very favourable conditions.

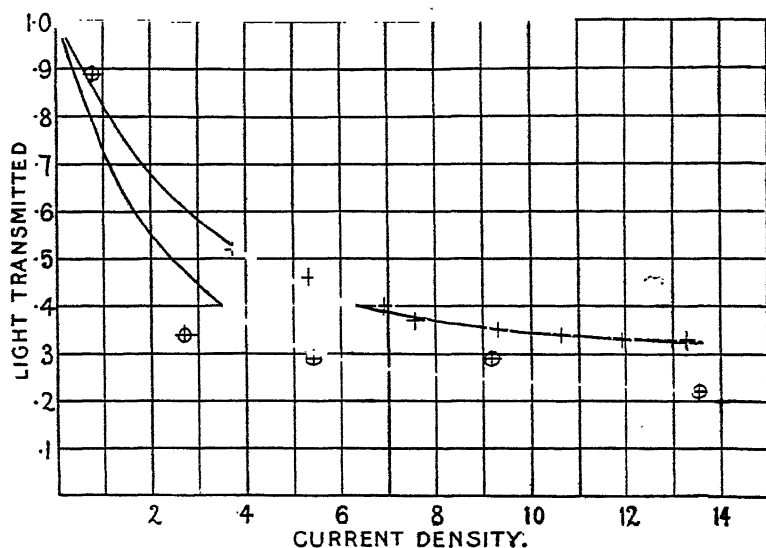


FIG. 3.

### *Measurements of Radiation.*

Previous workers have investigated the relationship of the amount of light radiated from the mercury vapour arc to the absorbing power of the luminous vapour when the power consumed in the absorbing arc is varied. They have thus connected values of the ratio (emission/absorption) with values of the power consumed. It has been thought that the results of these experiments suggests that part of the radiation is to be regarded as a temperature effect. We were led by these considerations to attempt to measure the intensity of the light radiated along the axis of our absorbing column and to connect it with the current density in the absorbing column. This was done with the same photometer arrangement as already described, the radiating arc at Q being of course extinguished. By suitable optical arrangements, the light passing through the lens  $L_2$  was made to produce a uniform illumination over the photometer screen. On account of the feebleness of the illumination it was found necessary to cut down the illumination from the comparison lamp by means of a narrow horizontal slit, which permitted only the light from a short length of the vertical vapour lamp to pass through. Typical measurements of the axial radiation of wave-length 5461 Å.U. are given in Tables III, IV, and V. The unit of illumination is arbitrary and is only approximately the same for the three Tables.

Table III.—Length of Column 13 cm.

Current density. Milliamps. per sq. cm.	Relative illumination.
5.5	1.0
8.2	1.8
11.0	2.8
13.7	4.0

Table IV.—Length of Column 35 cm.

Current density. Milliamps. per sq. cm.	Relative illumination.
8.1	2.0
9.1	2.4
10.8	3.0
11.9	3.6
13.5	4.0
14.8	4.6
16.4	5.2
21.4	7.4

Table V.—Length of Column 52 cm.

Current density. Milliamps. per sq. cm.	Relative illumination.
3.4	0.8
4.0	0.9
5.4	1.3
7.0	1.7
8.1	2.2
10.0	2.8
13.5	4.0
16.3	5.0

The results given in Tables III, IV, and V are shown graphically in fig. 4. The shapes of the curves distinctly suggest a linear relationship between current density and emission, except in the case of the 13-cm. column, where the curve is slightly concave upwards.

The intensity of the radiation emitted along the axis from the end of a uniform tube containing a luminous and absorbing medium is given by the expression  $(I/a)(1 - e^{-al})$ , where  $I dx$  represents the intensity of the radiation from a layer of thickness  $dx$ ,  $a$  the coefficient of absorption, and  $l$  the length of the tube. When  $al$  is large, the radiation is simply  $I/a$ . Thus the

curves obtained show that the relation between the ratio  $I/a$  and the current density is linear, the slight initial concavity being due to the influence of the second term in the expression.

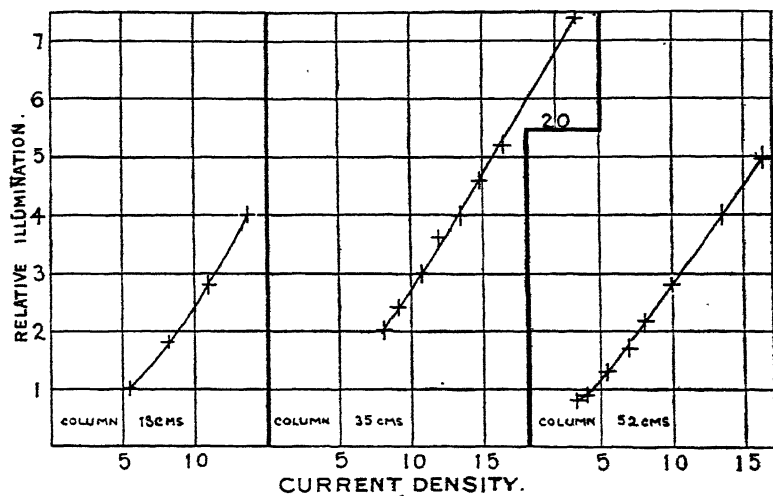


FIG. 4.

This result resembles to some extent that arrived at by L. Grebe from experiments on the absorption of the light from one mercury vapour lamp carrying a large current by a second vapour lamp, also carrying a large current. The important difference exists between Grebe's method of attacking the subject and that employed by us, that in our experiments the current densities used are so low, and the additional power developed in the column to render it luminous is so small compared with that required to keep up the temperature of the tube (*i.e.*, that developed in the heating coil and the ionising arc), that the temperature may be regarded as constant, and not depending on the illuminating current; whereas, in Grebe's work, an increase of temperature proportional to the power developed in the lamp was assumed. The power developed by our absorption current was never greater than 9 watts, while in Grebe's experiments the power in the absorption current ranged between 116 and 517 watts. In our experiment the temperature indications of the thermo-couples remained unaltered throughout a series of observations. We are forced to conclude that, under the conditions of our experiments, the increase of radiation is not to be ascribed to increase of temperature.



*Absorption of other Lines.*

Our photometric observations were confined to the green line (5461 Å.U.). We did, however, make an attempt to gain an idea of the extent to which light of other wave-lengths is absorbed by the luminous vapour. Photographs were taken with a concave grating spectrograph of 10 feet radius of the spectrum of the light from a silica mercury vapour lamp which passed through the experimental tube. Two spectra were photographed on the same film, the girder being slightly displaced between the two exposures. One exposure was made with the vapour column non-luminous; the second, of equal length, with the vapour luminous. Inspection of the developed film showed that the different mercury arc lines suffered very variable amounts of absorption. The results of this experiment are tabulated in Table VI.

Table VI.

## I. Lines Perceptibly Absorbed.

Å.U.		
5461	strongly	} First triplet ( $m = 2.5$ ) of the second subordinate series of triplets.
4359	"	
4047	"	
3342	very strongly	First member of second triplet of above series.
3663	strongly	} First triplet ( $m = 3$ ) of the first subordinate series of triplets.
3132	very strongly	
2967	"	
Å.U.		Å.U.
5289	slightly.	3650 strongly.
5295	"	3342 very strongly.
5308	"	3126 "
3655	strongly.	

## II. Lines not Perceptibly Absorbed.

Å.U.	
5791	} Lines ( $m = 3, 4, 5$ ) of Paschen's first subordinate series of single lines.
4347	
3907	
4916	Third line ( $m = 3.5$ ) of second subordinate series of single lines.
5770	} Lines of Paschen's combination series.
4339	
4078	
5068	
3984	

These results are, of course, to be regarded only as rough indications of the extent to which the various lines are absorbed. It is very probable that photometric measurements would show some degree of absorption in most of the lines given in the second list. In the case of 2536 Å.U., which is absorbed by non-luminous mercury vapour, the absorption is not apparently increased when the vapour is rendered luminous. Though the yellow lines (5791 Å.U. and 5770 Å.U.) are two of the brightest lines in the mercury arc spectrum, they are not strongly absorbed. With regard to these two lines, our experience is much at variance with that of Pflüger,\* who records a heavy absorption for both of them. The divergence between our respective results may be due to the great difference of the conditions, Pflüger's work having been conducted with absorbing arcs of large current density.

Kuch and Retschinsky deduced the existence of absorption in the case of some of the ultra-violet lines from a comparison of photographs of the spectra of the radiation from the ends of short and long columns of luminous mercury vapour. In Table VI above we have now direct evidence of absorption of ultra-violet lines.

*Application of the Stewart-Kirchhoff Law to Bright Line Radiation.*

Previous workers have given much attention to the question of the applicability of the Stewart-Kirchhoff law, or a modification of that law, to the line radiation from luminous gases. This law holds rigorously in the case of pure temperature radiation (such, for example, as the radiation from  $\text{CO}_2$  at  $\lambda = 4.3 \mu$ ).

If the radiation from a source between the wave-lengths  $\lambda$  and  $\lambda + d\lambda$  be  $E d\lambda$ , and its absorption for the same range of wave-length be  $a$ , then

$$\frac{E d\lambda}{a} = I d\lambda, \quad (1)$$

where  $I d\lambda$  represents the radiation of a black body for that range at the temperature of the actual radiating body. This states the law for pure temperature radiation. For other than pure temperature radiation,  $I d\lambda$  represents the radiation, for that range, of a black body at the "emission temperature," the emission temperature being the temperature at which the emission of a black body is equal to the ratio of the emission to the absorption of the radiating body.

Imagine two ordinary mercury vapour lamps, emitting the same spectral lines, so placed that the radiation from one, P, passes through the other, Q.

\* 'Ann. der Phys.,' vol. 26, p. 805 (1908).

Let us consider a single line, of which the widening is due entirely to the temperature Doppler effect. This supposition is warranted, in the case of gases at low pressure, by the experimental results of Michelson and of Buisson and Fabry.

For the energy distribution in a spectral line emitted by a gas we have

$$E d\lambda \propto dN \propto e^{-u^2/2R\theta} du = e^{-\beta u^2} du, \quad (2)$$

where  $dN$  is the number of molecules whose velocities resolved in the line of sight lie between  $u + du$ ,  $R$  is the gas constant, and  $\theta$  the absolute temperature.

If  $\lambda_0$  is the wave-length corresponding to the middle of the line, and  $\lambda$  the wave-length corresponding to a velocity  $u$  in the line of sight, then

$$\lambda = \lambda_0 \left(1 + \frac{u}{c}\right), \quad (3)$$

where  $c$  is the velocity of light and

$$du = \frac{c}{\lambda_0} d\lambda.$$

Substituting in (2), we have

$$E d\lambda \propto \frac{c}{\lambda_0} e^{-k(\lambda - \lambda_0)^2} d\lambda,$$

where

$$k = \beta \frac{c^2}{\lambda_0^2},$$

or

$$E d\lambda = E_0 e^{-k(\lambda - \lambda_0)^2} d\lambda, \quad (4)$$

where  $E_0$  is the intensity in the middle of the line. For the radiation between  $\lambda$  and  $\lambda + d\lambda$  from the lamp Q we have

$$E d\lambda = E_q e^{-k_q(\lambda - \lambda_0)^2} d\lambda, \quad (5)$$

and for that from the lamp P,

$$E' d\lambda = E_p e^{-k_p(\lambda - \lambda_0)^2} d\lambda. \quad (6)$$

The radiation within this range of wave-length which is emitted by P and absorbed by Q is

$$a E_p e^{-k_p(\lambda - \lambda_0)^2} d\lambda,$$

where  $a$  is the absorption, *i.e.*, the fraction of the incident light which Q absorbs.

From (1) and (5)

$$a = \frac{E_q}{I} e^{-k_q(\lambda - \lambda_0)^2},$$

so the radiation absorbed is given by

$$ds = \frac{E_p E_q}{I} e^{-(k_p + k_q)(\lambda - \lambda_0)^2} d\lambda.$$

Integrating over the whole width of the line, we have for the radiation absorbed by Q

$$s = \frac{E_p E_q}{I} \int_{(\lambda - \lambda_0) = -\infty}^{(\lambda - \lambda_0) = \infty} e^{-(k_p + k_q)(\lambda - \lambda_0)^2} d\lambda = \frac{E_p E_q}{I} \sqrt{\left(\frac{\pi}{k_p + k_q}\right)}. \quad (6A)$$

The light radiated by P is given by

$$S_p = E_p \int_{(\lambda - \lambda_0) = -\infty}^{(\lambda - \lambda_0) = \infty} e^{-k_p(\lambda - \lambda_0)^2} d\lambda = E_p \sqrt{\left(\frac{\pi}{k_p}\right)}. \quad (7)$$

Therefore,

$$\frac{s}{S_p} = \frac{E_q}{I} \sqrt{\left(\frac{k_p}{k_p + k_q}\right)} = A. \quad (8)$$

This ratio A is what is actually measured in experiments on the absorption of a single line radiation.

The emission from the lamp Q is given by

$$S_q = E_q \sqrt{\left(\frac{\pi}{k_q}\right)}. \quad (9)$$

Therefore the ratio (emission/absorption) of Q, as measured, is

$$\frac{S_q}{A} = I \sqrt{\left(\pi \left[\frac{1}{k_p} + \frac{1}{k_q}\right]\right)}. \quad (10)$$

Substituting for  $k$  the value

$$\beta \frac{c^2}{\lambda_0^3} = \frac{1}{2R\theta} \cdot \frac{c^2}{\lambda_0^3},$$

$$\frac{S_q}{A} = \frac{\lambda_0}{c} I \sqrt{(2\pi R[\theta_p + \theta_q])}, \quad (11)$$

or,

$$A = \frac{c}{\lambda_0} \frac{S_q}{I} \sqrt{\left(\frac{1}{2\pi R[\theta_p + \theta_q]}\right)}, \quad (12)$$

where  $\theta_p$  and  $\theta_q$  are the absolute temperatures of the vapour in P and in Q respectively.

From this it appears that in the case of pure temperature radiation, or of radiation following the modified form of the Stewart-Kirchhoff law, referred to above, the conditions in the absorbing vapour being maintained constant, an increase of temperature in the radiating arc will diminish the coefficient of absorption as measured. It is easy to see that this must be so, since the increase of temperature will widen the radiated line, the absorption line remaining of constant width. In fact, any cause which will widen the radiated line will decrease the coefficient of absorption, because a greater proportion of energy will be radiated in the outer parts of the widened line, where the absorption is less than in the middle. To test this conclusion, we made some experiments in which the widening of the radiated line was

produced by increasing the current in the radiating arc. The results are given in Table VII.

Table VII.

Current density in absorbing column. Milliamps. per sq. cm.	Current in radiator amps.	Absorption A.
14	{ 1.5	0.71
	{ 3.0	0.58
7	{ 2.0	0.56
	{ 3.0	0.48

These results show definitely that, when the absorption is as sharply selective as that we are now discussing, the absorption coefficient for a single line radiation (as usually measured) depends on the conditions in the radiator as well as those in the absorber.

The complexity of a spectral line must have a great influence on the apparent absorption of the line, if the modified Stewart-Kirchhoff law holds. For example, let  $W_1$  and  $W_2$  be two neighbouring lines radiated by the lamp P and absorbed by the lamp Q. Of these lines, suppose that  $W_1$  is made up of two close components of equal intensity, actually separate and not overlapping, but too close for resolution by the apparatus employed to observe them. Let the complex line  $W_1$  and the single line  $W_2$  appear equally bright. Then the absorption of each member of the doublet  $W_1$  may be taken as  $A$  (see equation 11, above) and the emission of each as  $S_p$ . The light absorbed by Q from each member will be  $AS_p$ , so that the total light absorbed from  $W_1$  will be  $2AS_p$ . The emission of the single line  $W_2$  will be  $2S_p$ , and if the modified form of the Stewart-Kirchhoff law holds, the absorption of the line  $W_2$  will be  $2A$ . So that the light absorbed from the single line will be  $2A2S_p$ . Thus the absorption of the line  $W_2$  will appear to be double that of  $W_1$ , the ratio emission/absorption of each component of  $W_1$  being the same as that of  $W_2$  (see equation (11) above)). It is evident that the modified form of the law will fail if  $W_1$  and  $W_2$  are treated as two single lines, whereas it will hold if the two components of the doublet  $W_1$  and the single line  $W_2$  are treated (as they should be treated) as three separate lines.

A possible example of the application of these considerations may be supplied by the case of the two bright yellow mercury lines. Of these, Pfüger states that 5790 Å.U., the brighter, is less absorbed than 5770 Å.U., the less bright. But even though  $(E/a)$  were constant throughout the structure of both lines, this might be the case if the brighter line were more complex than the other. It is interesting to observe that Prof. R. W. Wood's

photographs of the two lines\* show that the line 5790 Å.U. is very much more complex than 5770 Å.U.

*On the Reversal of the Mercury Lines.*

Many of the mercury lines have been observed to be self-reversed in the spectrum of the unenclosed mercury arc at atmospheric pressure. Perott† records an observation of the self-reversal of the main component of the green line from a mercury vapour lamp viewed end-on, with an air étalon of 1 cm. thickness.

Our own study of the reversal may be divided into two parts: the first part consisted of experiments with a silica mercury vapour lamp as the source of radiation; the second of an attempt to produce a reversed dark line on the continuous background of the white light spectrum of a carbon arc, and, later, on the solar spectrum. In all these experiments, the absorption took place in the low current arc already described.

In the first series of experiments, the light from the silica lamp was made to pass, as before, through the experimental tube in a parallel beam, being then brought to a sharp focus by the lens  $L_2$  on to a small hole drilled in an opaque screen. Close behind the screen was placed a glass plate étalon of 5 mm. thickness. In this way the effect of the diffuse illumination from the absorbing column was minimised. The ring system was observed, as usual, through a small telescope. A green-ray filter was placed between  $L_2$  and the perforated screen. If the pressure in the radiator arc is small, the appearance of the rings is as shown in (Plate 3, fig. 5a), which is from a photograph taken with the actual apparatus. In this photograph, besides the main line system, two satellite systems are seen. One of these is  $\lambda + 0.09$  Å.U., the rings of which lie just within the corresponding main line rings. The other is  $\lambda - 0.07$  Å.U.; its rings lie just outside the corresponding main line rings.

For the purpose of the reversal experiments, we used a rather higher pressure in the radiator, thus widening the lines slightly. The appearance of the rings under the higher pressure is shown in the right-hand half of fig. 5b. On gradually increasing the current in the absorbing column from a very low value, the following series of changes in the appearance of the ring system takes place. At first, with the lowest current, the main line rings become darker. As the absorbing current increases, a fine dark line appears in each main line ring. At this stage, the split main line and the satellite  $\lambda - 0.07$  Å.U. appear like three close lines, somewhat resembling a Zeeman triplet. After this the absorption dark line broadens,

\* 'Phil. Mag.,' vol. 25, p. 443 (1913).

† 'Comptes Rendus,' vol. 148, p. 404 (1909).

and the general diminution of brightness of the main line system, together with the absence of appreciable absorption of  $\lambda - 0.07 \text{ \AA.U.}$ , renders the line of demarcation between the main line and  $\lambda - 0.07 \text{ \AA.U.}$  less distinct. This gives an appearance of asymmetrical reversal of the main line.

This stage is represented in the left-hand half of fig. 5b. Looking at the photograph, we see in the left-hand half a series of pairs of strong dark lines. The outer line of each of these pairs is the reversed absorption line. It will be seen that each of these absorption lines corresponds to a bright line in the right-hand half of the figure. Each absorption line is bounded by two bright lines, of which the inner bright line is the unabsorbed edge of the widened main radiation line; the outer bright line is made up of the other edge of the main radiation line and the satellite  $\lambda - 0.07 \text{ \AA.U.}$ , which coalesce. Outside, and very close to this latter line, is the satellite  $\lambda + 0.09 \text{ \AA.U.}$  If the pressure in the radiating arc is kept very low by means of a liquid air-cooled charcoal bulb, the main radiation line is so narrow that the unabsorbed edges are not visible; and gradually increasing the absorbing current merely has the effect at first of progressively diminishing the brightness of the main line system until the satellite systems alone remain visible.

The green line  $5461 \text{ \AA.U.}$  is a group consisting of at least seven lines. The reader is referred to the beautiful photograph of the group by Prof. McLennan.\* We have photographed the line with a small échelon of twelve 1 cm. plates, using the light radiated along the axis of our absorbing column, the spectro-scope slit being placed sufficiently far from the end of the column to ensure that all parts of the column should be nearly equally effective. With a column length of 52 cm. and a current density of 0.3 ampère per square centimetre, all the light being thrown into one order of the échelon, the brightness of the satellites was seen to be very greatly enhanced, so that they became hardly distinguishable in brightness from the main line itself. The equalisation of the brightness of the satellites under these conditions points to the existence of absorption in the case of the brighter members of the group, and suggests the possibility of the reversal of some of the brighter satellites. This consideration led us to search for reversals of satellites and we succeeded in observing the reversal of  $\lambda + 0.09 \text{ \AA.U.}$  For this we employed the same arrangement of the étalon as was used for observations on the main line reversal, with which the photographs fig. 5b were taken. A widened line was produced by admitting air into the radiator arc. A large image of the ring system was formed by a long focus lens and a pointer was adjusted to the position of one of the satellite rings. The region round the pointer was

\* 'Proc. Roy. Soc.,' A, vol. 87, Plate 4, fig. 1.

examined with an eye-piece. On switching on the 52-cm. absorbing column current, a dark ring appeared on the pointer. The pointer is necessary on account of the complexity of the reversal pattern, the main line itself being, of course, reversed. This observation of the reversal of a satellite supports the conjecture that multiple reversals such as are observed in the lines of metal arc spectra may be due to reversals of satellite lines.

The reversal experiments just described were all carried out with a bright vapour lamp as radiator. The results of these experiments suggested an attempt to produce an absorption spectrum of the luminescent vapour on the white light spectrum of an ordinary carbon arc. For this we used a concave grating of 10 feet radius and 45,000 lines. The line was seen reversed in the first order. We succeeded in reversing the line 5461 Å.U. and 4359 Å.U. on the carbon arc spectrum. We reproduce a photograph of the reversed green line on the background of the solar spectrum. The photograph was taken in the second order. In fig. 6, Plate 3, two photographs of the solar spectrum in this region are placed in juxtaposition, one showing the reversed mercury line. A wave-length scale graduated in single Å.U.s is attached. These two photographs were taken under the same conditions, except that in the case of one of them the column of mercury vapour traversed by the solar light was made luminous by the passage of a small current.

The reversal of the green line on a continuous spectrum forms a very striking experiment. To see it, an absorbing arc of 10 cm. length or more should be used, and the absorption tube should have been well exhausted with the liquid air-cooled charcoal. The white-light background spectrum being bright, the reversed line appears on closing the absorbing arc circuit. The reversal can be seen with a current density of only 1/10 milliampère per square centimetre in the 52-cm. column. A slightly higher current, however, produces a better defined line. It is possible to reverse the line on the continuous spectrum of a tungsten filament lamp.

Reference has already been made to the pinkish tint of the light emitted by the absorbing column when observed along the axis of the tube. This, of course, is due to the heavy absorption of the bright green and blue lines and to the enhancement of the red and yellow radiations due to the length of the radiating column combined with low absorption. The pink tint is characteristic of low current density discharge. As the current density increases, the light radiated along the axis of the tube regains the usual colour of the mercury arc.

Our observations on the reversal of the green line show that the absorption is greatest in the middle of the line and falls off on either side. The effect of this is to increase the brightness of the edges of the radiation line



relatively to the middle when the light is radiated along the axis of a long column. In other words, the radiation line seen along the axis of a column is wider than that emitted from the side of a narrow tube. This is the fifth cause of widening enumerated by Lord Rayleigh.\* He observes that "It must certainly operate, but does not appear to be important in practice." Examination of the group 5461 Å.U., with the twelve-plate échelon along the axis of our 52-cm. column, with a current density of 0.2 ampère per square centimetre, showed the lines less sharp than those from an ordinary low pressure lamp. Whether this effect is really due to the cause of widening alluded to above, or whether it is to be attributed to the increased brightness of the satellites is not certain, the resolving power of the échelon being hardly sufficiently high to warrant a definite conclusion. It is possible that an instrument of higher resolving power would definitely reveal the existence of this kind of widening in the lines radiated from the ends of long columns of vapour of low density, such as we have employed.

#### *Summary.*

1. Experiments are described in which mercury vapour at low pressures, rendered luminous by the passage of small electric currents, is found to exert powerful selective absorption.

2. A list of wave-lengths found to be absorbed is given. It is found that, of the series lines, those belonging to the first and second subordinate series of triplets exhibit heavy absorption.

3. Photometric observations are recorded on the absorption and emission of 5461 Å.U. by columns of mercury vapour of different lengths and carrying different currents.

4. The relation between the ratio (emission/absorption) and the current density is found to be linear.

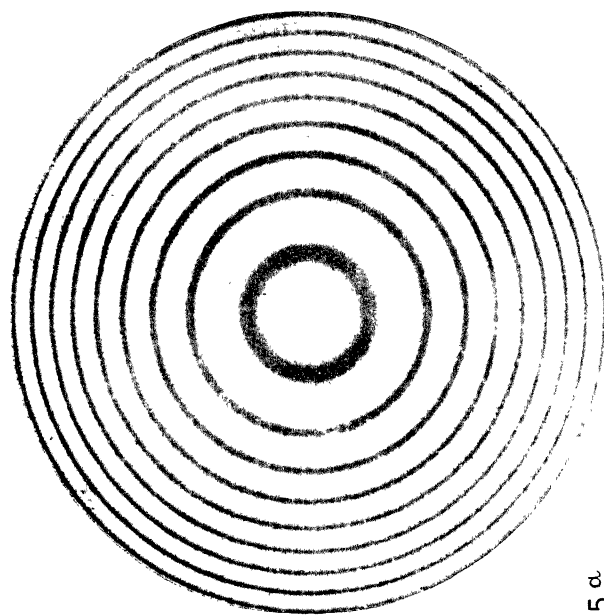
5. The applicability of the Stewart-Kirchhoff law to bright-line radiation is discussed; and it is shown that the complexity of a line may have a great influence on its absorption.

6. The lines 5461 Å.U. and 4359 Å.U. have been reversed, so as to appear as dark lines on the white-light spectrum of a carbon arc and of the sun.

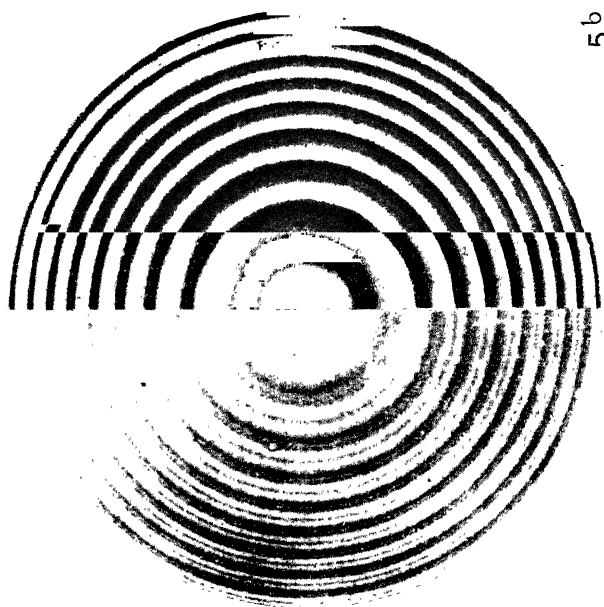
7. The reversal of 5461 Å.U. has been studied in detail with a Fabry and Perot étalon and with an échelon spectroscope.

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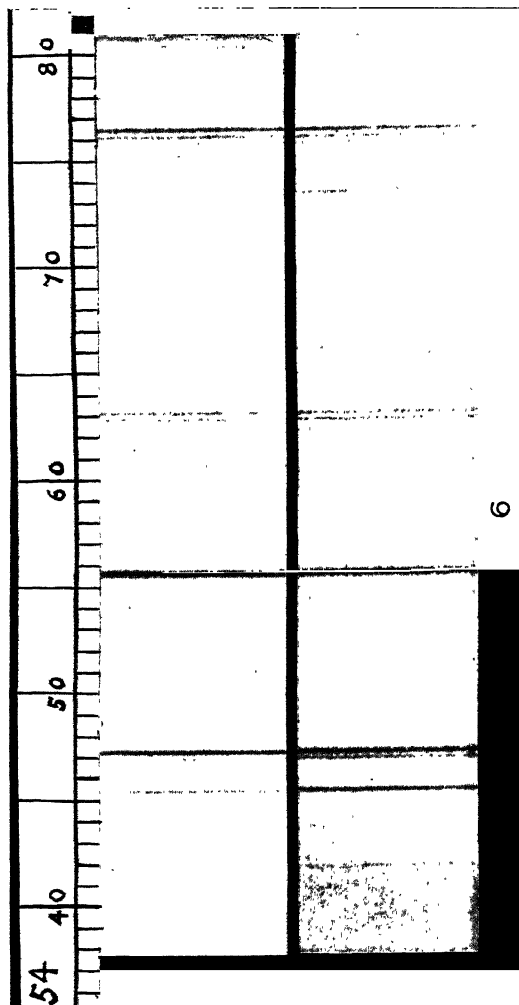
\* 'Phil. Mag.,' vol. 29, p. 274 (1915).



5<sup>a</sup>



5<sup>b</sup>



6



*Revision of Series in the Arc Spectrum of Mercury.*

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(Communicated by Prof. A. Fowler, F.R.S.—Received June 23, 1921.)

[PLATES 4 AND 5.]

*Introductory.*

The generally accepted analysis of the arc spectrum of mercury into series is scattered throughout a number of papers by Paschen\* and a paper by Wiedmann.† It shows the spectrum to contain a triplet and a singlet system of lines. Each system comprises the four main types of series—principal, diffuse, sharp and fundamental—and there are combinations and intercombinations among the systems. The scheme is partly collected by Dunz,‡ and again by McLennan,§ but in neither case is the complete arrangement given, so far as it is understood at present. Such a collection presents some difficulty, especially with regard to the diffuse triplet and singlet series and their combinations. Wiedmann gives the diffuse triplet series in such a form that the three components of a triplet, with satellites, contain respectively 3, 3 and 2 lines, instead of the customary 3, 2 and 1 lines. With this classification, he draws attention to a remarkable frequency difference relation between this series and the diffuse singlet series and its combinations. But, if this arrangement is adopted, the strong series of chief lines of the first components of the triplets, as given by Dunz, is left unaccounted for. It is possible, moreover, to retain Dunz's triplet, which has the ordinary form, and, by designating the then outstanding lines of Wiedmann's triplet as lines of combination series, to make the aforesaid frequency-difference relation a necessary result. This arrangement appears, on the whole, to be the better of the two. It has, however, the disadvantages that it involves the splitting up of what appear to be close associated groups of lines into members of different series, and, further, that it gives combination series,  $2P-md''$ ,  $2P-md'$ —both consisting of very strong lines—without a trace of the corresponding series,  $2P-md$ , arising from the first chief line of the triplet.

\* 'Ann. d. Phys.,' vol. 29, p. 662 (1909); vol. 30, p. 750 (1909); vol. 35, p. 869 (1911); 'Jahrb. der Rad. und Elek.,' vol. 8, p. 178.

† 'Ann. d. Phys.,' vol. 38, p. 1041 (1912).

‡ 'Dissert. Tübingen,' 1911.

§ 'Roy. Soc. Proc.,' A, vol. 87, p. 256 (1912).

*Suggested Rearrangement in Quadruplets.*

In the present paper a new arrangement is attempted, which overcomes these difficulties. The triplets are associated with certain singlet series, and converted into quadruplets. It will be seen from the Tables which follow that, so far as numerical relations are concerned, the evidence for the recognition of quadruplets is complete. The characters of the lines, also, in the series which have been brought together, are quite in keeping with such association. The lines of the principal triplet series are said by Wiedmann to resemble in appearance those of the series with which they are here associated so closely as to be almost indistinguishable from them. He finds the distinction, however, in the fact that the latter lines are shaded towards the violet, while the triplets are shaded towards the red. In the case of the diffuse quadruplets, the added component, consisting of three lines, contains what is usually regarded as the diffuse singlet, and a pair of combination lines, which are equally strong and diffuse. The new component of the sharp quadruplet is described by Wiedmann as being particularly sharp. It appears, therefore, that there are strong reasons for supposing that we have in mercury a system of quadruplet series.

Quadruplet series have not so far been observed in any other spectrum. A number of quadruplets (groups of four lines having constant frequency differences) have been detected in the red spectrum of argon, but they have not been arranged in series, nor are the frequency differences related to one another in the same way as those of an ordinary series triplet or a mercury quadruplet. The present arrangement, therefore, introduces a new type of series. On this account, it has been thought advisable to employ Greek capital letters as symbols for the limits and terms, in order to distinguish them from those of the older established types.\*

In the arrangement suggested, the spectrum consists of series of quadruplets and singlets. Five singlet series are recorded, including principal, diffuse, sharp, and two combination series. The three main series have been identified on the ground that they show the customary relations between the limits of such series. These relations can be satisfied also by a different selection, namely, the P, D and S series may be respectively Nos. IV, III and II, as numbered in the Tables. The former arrangement, however, seems more suited to the character of the lines. It will be observed that, with the exception of the series of terms  $mP$ , the whole of the singlet system can be derived from the quadruplets. If, therefore, the origin of the  $mP$  terms

\* The terms of triplet systems are usually denoted by small Latin letters ( $p, d, s, f$ ), those of doublets by small Greek letters ( $\pi, \delta, \sigma, \phi$ ), and those of singlets by Latin capitals (P, D, S, F).

could be found in the quadruplet system, the whole group of singlet series would become combinations, and the spectrum, so far as it is classified, would consist entirely of a quadruplet system and its derivatives. It has not been found possible so to explain the  $mP$  terms, however, so that, for the present, it seems best to regard the singlets as having a partially independent existence. In this connection, the following relations, while of no obvious significance at present, may be of some interest in view of possible future indications of a relation between the quadruplets and the  $mP$  terms:— $2P-4P = (1\Sigma-2\Pi_3) + (1\Sigma-2\Pi_4)$ ;  $3P-5P = 3\Sigma$ ;  $2P-5\Pi_1 = 1\Sigma-4\Pi_2$ .

*Structure of the Diffuse Series.*

The diffuse quadruplet series calls for special attention, on account of its complicated structure. It will be seen from the Tables that, in the first member of the series, the four components contain, respectively, 3, 4, 3, 2 lines. It is customary, in complex series of this type, to select, from each component, one line, known as the chief line, while the others are classed as satellites. The chief line is usually the strongest of its group, and, in the first two components, is displaced in the direction of shorter wave-length by a satellite, which takes part in the constancy of frequency interval characterising diffuse doublet and triplet series. This, however, is by no means a universal rule. In selenium and manganese, for instance, there are decided anomalies. In the case of the mercury quadruplets also, no such simple separation into chief lines and satellites appears to be possible. It is probably better, therefore, to regard each component as being a complex group of chief lines, containing, respectively, 3, 4, 3, 2 lines, as already mentioned. This interpretation receives some support from the fact that, in the third and subsequent members of the series, fainter lines make their appearance in the second component of the quadruplet—one on either side of the main group. In the third quadruplet there is also an extra companion on the side of shorter wave-length—which may, indeed, be present, though unresolved, in the following members. These fainter lines, which are printed in italics or underlined in the Tables, might well be regarded as satellites. They are given here for the first time, having been detected and measured on an excellent plate taken by Mr. F. S. Phillips in the Spectroscopic Laboratory at the Imperial College of Science and Technology, by a method to be described later. The plate, with the analysis of the spectrum into series, is reproduced in Plate 4. In Plate 5 a portion of the spectrum is given on a larger scale, which brings out very clearly the second components of the higher members of the diffuse and sharp quadruplets. The second member of the diffuse quadruplet series is shown completely on the same plate,

together with the interpretation of the lines on what has been referred to in the first paragraph as probably the better of the two existing views of the structure of the series. The second component of the third member also is there reproduced, with satellites which have no equivalent in the corresponding component of the second member.

The complex nature of the diffuse quadruplet series has its effect on the derived fundamental series. It will be seen that the first diffuse quadruplet has four "terms"— $m\Delta'''$ ,  $m\Delta''$ ,  $m\Delta'$  and  $m\Delta$ . There should, therefore, be a fundamental series of quadruplets, if the proposed arrangement is correct. This series has been found, and its "terms,"  $m\Phi$ , take part also in a combination series with the limits of the subordinate quadruplet series.

[*Note added July 28, 1921.*—Since this paper was written, all but one of the series of lines,  $1\Pi_2 - m\Delta_1$ , described as "satellites," have been identified as the combinations  $1\Pi_2 - m\Pi_2$ . Thus,  $1\Pi_2 - 5\Delta_1$  should be  $1\Pi_2 - 5\Pi_2$ , and so on for all higher members of the series. The line  $1\Pi_2 - 4\Delta_1$ , however, is not identical with  $1\Pi_2 - 4\Pi_2$ . The latter combination would be  $\nu = 35533\cdot6$ , or  $\lambda = 2813\cdot42$ , which differs by nearly 3 Å.U. from the measured line. There appears, therefore, in this case, to be an actual satellite.

Mr. Takamine, of Tokyo, has suggested to the author that the second series of "satellites,"  $1\Pi_2 - m\Delta_2$ , may be the combinations  $1\Pi_2 - m\Phi$ . The combinations  $1\Pi_2 - 3\Phi$  and  $1\Pi_2 - 4\Phi$  are already included in the Tables with the quadruplet series  $1\Pi_{1,2,3,4} - m\Phi$ . The remaining  $m\Phi$  terms are not known, but extrapolation by means of a Hicks formula gives the following results, which strongly support the suggestion of Mr. Takamine:—

<i>m.</i>	Extrapolated values of $m\Phi$ .	Combination, $1\Pi_2 - m\Phi$ .	Observed lines, classed as $1\Pi_2 - m\Delta_2$ .
		<i>ν.</i>	<i>ν.</i>
5	3074	37064	37063·5
6	2256	37882	37884·2
7	1726	38412	38415·1]

#### *Discussion of the New Arrangement.*

The chief objection to the new arrangement of the mercury spectrum seems to be that it has no analogue in the spectra of the chemically-related elements zinc and cadmium. There is, however, so far as we know, no fundamental necessity for an element to follow the course of the earlier members of its group in the periodic table. In both its physical and chemical properties mercury shows wide divergences from zinc and cadmium, which exceed, in

fact, those we might expect from the possible absence of an element between zinc and cadmium in the family group. There appears to be no reason why such divergences should not characterise the spectrum also. In some respects they are known to do so. For example, in the alkalis and alkaline earths, the limits of all the principal, sharp and diffuse series that occur (taking the first components of doublets and triplets) decrease in wave-number as we proceed along the family from the lighter to the heavier elements. Zinc and cadmium show the same tendency, but in mercury, in all cases except that of the diffuse and sharp triplets (here, diffuse and sharp quadruplets), the limits are higher than the corresponding ones of cadmium. A similar decrease characterises also the ionisation potentials of the alkalis, alkaline earths, and zinc and cadmium—but fails again when we come to mercury. It appears, therefore, that novel features in the structure of the mercury spectrum are not to be altogether unexpected. The reality of the quadruplets is enhanced in probability when we consider the conditions that have to be fulfilled in order to construct them from a triplet system. There must be a singlet series having the same limit ( $1s$ ) as the principal triplets; two singlet series, having identical limits, and the same terms ( $ms$  and  $md$ ) as the sharp and diffuse triplets, respectively; and possibly series with terms  $md'$ ,  $md''$ . The lines of the first of these series (having the limit  $1s$ ) must lie on the opposite side of the principal triplets to that occupied by the lines of the other two required singlet series with relation to the respective subordinate triplets. Also, the difference between the limit of the first series and the wave-number of its first member must be the common limit of the other two series. In our ignorance of the principles underlying the association of triplet and singlet series, the chance that these conditions will all be fulfilled in the same spectrum appears to be very small. They are, in fact, not even approximately satisfied in any known spectrum other than that of mercury, except the spectrum of cadmium. Here they partially hold, but not at all completely, and the distances between the triplets and such of the required singlet series as exist are so great, compared with the triplet separations, as to preclude any possibility of their association. This unique property of the mercury spectrum, against what appear to be heavy odds, affords strong evidence for the recognition of quadruplets. The probability is increased still further when we find that the separations of the components of the quadruplets are in the approximate ratio we should expect from our knowledge of triplets, and, moreover, that a fundamental series of quadruplets exists, as well as a quadruplet combination series. There is, in fact, precisely the same evidence here for the existence of quadruplet series as there is for recognising, in some other spectrum, the existence of triplets rather than doublets and singlets separately.



*Observation of New Series Lines.*

In the Tables that follow, all the measures are expressed on the International Scale. In the case of Paschen's infra-red lines, the values have been corrected in the manner pointed out by him\* on account of errors of calculation in the original values. Existing measures have been utilised as far as possible, but many of the lines included are now given for the first time. These have been measured from the plate already referred to, which was taken by means of a quartz Littrow spectrograph, giving a dispersion of

7.9 Å.U. per millimetre at  $\lambda 2400$  and 12.9 Å.U. per millimetre at  $\lambda 2800$ . The spectrum was produced by means of the apparatus illustrated in fig. 1. The mercury was contained in a long U-tube, having the left-hand limb prolonged into a wide quartz tube, into which a small cylinder of iron, pierced with a central hole, was fixed just above the level of the mercury. The quartz tube was connected to a pump, so that it could be exhausted. The mercury and iron cylinder were connected to the source of current, and the arc was struck by raising the right-hand limb of the U-tube until contact was established between the mercury in the left-hand limb and the iron. The upper part of the quartz tube was then exhausted, and the flame of the arc was thereby sucked through the hole in the iron into the space above. The spectrum shown in the Plates was due to this flame. It will

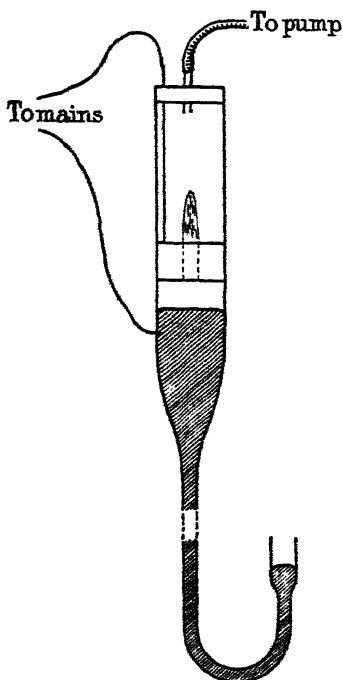


FIG. 1.

be observed that it consists almost entirely of series lines, which appear by this method to be produced free from the large number of unclassified lines which are present in the ordinary arc. On account of the smallness of the dispersion, and the nebulous character of many of the lines, the new measures are considered to have a maximum error of 0.03 Å.U. The sharp lines will probably have an error of less than this. A remarkable feature of the plate is that the line 2534.77 appears distinctly stronger than the resonance potential line 2536.52. Cardaun† gives the intensities of these lines as (4) and (10) respectively. The intensities

\* 'Ann. d. Phys.,' vol. 36, p. 197 (1911).

† 'Zeit. für Wiss. Phot.,' vol. 14, p. 89 (1915).

given in the Tables have, in a few cases, been adjusted, in order to preserve the true succession of intensity throughout a series. Different observers adopt different standards, and as Stiles\* remarks, the intensities of mercury lines vary greatly with the conditions of production of the spectrum. No alterations have been made, however, without verifying that the numbers given represent relatively the actual observations.

In the Tables, the wave-lengths and wave-numbers are denoted respectively by  $\lambda$  and  $\nu$ , and the "terms" by  $m\Pi$ ,  $m\Sigma$ , etc. The column headed  $\Delta\nu$  shows the wave-number separations of the components of quadruplets. In the diffuse series, the separations of the constituent lines of each component are also given under this heading. The value of  $1\Sigma$  has been obtained by correcting Wiedmann's figure (*loc. cit.*) to the International Scale. The other limits have then been calculated from observed lines in the usual way.

The newly-measured lines are indicated by footnotes.

The letters sometimes included with the intensities have the following meanings:— $n$  = nebulous,  $r$  = nebulous on red side,  $v$  = nebulous on violet side,  $R$  = easily reversed.

\* 'Astrophys. Journ.,' vol. 30, p. 48 (1909).

### Principal Quadruplets.

		Current Designation.	
$1\Sigma - m\Pi_1$	.....	$2\cdot5s - mP$	— Combination.
$1\Sigma - m\Pi_2$	.....	$2\cdot5s - mp_1$	} — Principal Triplets.
$1\Sigma - m\Pi_3$	.....	$2\cdot5s - mp_2$	
$1\Sigma - m\Pi_4$	.....	$2\cdot5s - mp_3$	
$1\Sigma = 21830\cdot8$			

$m$ .	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	$m\Pi$ .
1	—12070·23 —5460·74 (10) —4358·34 (10) —4046·56 (10)	—8282·7 —18307·5 —22938·1 —24705·4	10024·8 4630·6 1767·3	30113·5 40138·3 44768·9 46536·2
2*	? 11287·15 (10) 18673·09 (6) 13950·76 (2)	? 8857·3 7311·7 7166·2	— 1545·6 145·5	— 12973·5 14519·1 14664·6
3	6072·63 (5) 6907·53 (10) 7082·01 (4) 7092·20 (1r)	16462·9 14473·0 14116·4 14096·2	1989·9 356·6 20·2	5367·6 7857·8 7714·6 7734·4
4	5675·86 (5) 5803·55 (4r)† 5859·32 (4r)† 5872·12 (2)	17614·5 17226·1 17062·1 17025·0	388·4 164·0 37·1	4216·3 4604·7 4768·7 4805·8

## Principal Quadruplets—(continued).

<i>m.</i>	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	<i>m</i> $\Pi$ .
5	5316·69 (3r)	18803·6		3027·2
	5354·05 (4r)	18672·4	131·2	3158·4
	5384·70 (3r)§	18566·1	106·3	3264·7
	5389·01 (1)	18551·2	14·9	3279·6
6	5102·42 (2r)	19593·1		2237·7
	5120·65 (3r)	19523·4	69·7	2307·4
	5138·09 (1)	19457·1	66·3	2373·7
	5140·10 (1)	19449·5	7·6	2381·3
7	4970·13 (1r)	20114·7		1716·1
	4980·82 (3r)	20071·5	43·2	1759·3
	4991·5 (2)	20028·5	43·0	1802·3
	—	—	—	—
8	4883·1 (1)	20474·5		1356·3
	4890·27 (2r)	20443·1	31·4	1387·7
	4896·9 (1)	20415·4	27·7	1415·4
	—	—	—	—
9	4822·3 (1)	20731·3		1099·5
	4827·1 (2)	20710·7	20·6	1120·1
	4832·2 (1)	20688·8	21·9	1142·0
	—	—	—	—
2nd component only.				
10	4782·1 (1)	20905·6		925·2
11	4748·1 (1)	21055·2		775·6
12	4722·8 (1)	21168·0		662·8
13	4701·8 (1)	21262·5		568·3
14	4685·3 (1)	21337·3		493·5
15	4672·7 (1)	21394·8		436·0
16	4662·4 (1)	21442·3		388·5
17	4653·4 (1)	21483·8		347·0

\* Paschen ('Ann. d. Phys.,' vol. 35) hesitates between this triplet and (12390·7), 13950·76, (?) — the latter being indicated by a Hicks formula. The line  $1P-2\Pi_3$ , however, afterwards discovered by Woolf, indicates that the triplet given in the Table is the true one.

† This line occurs also as  $2P-5\Pi_1$ . It is very diffuse, and is considered by Paschen to arise from both sources.

‡ Has satellites 5860·10 and 5868·08.

§ Has satellite 5385·79.

Sharp Quadruplets.

$1\Pi_1 - m\Sigma$ .....	Current Designation.
$1\Pi_2 - m\Sigma$ .....	$2P - ms$ — Combination.
$1\Pi_3 - m\Sigma$ .....	$2p_1 - ms$ } — Sharp Triplets.
$1\Pi_4 - m\Sigma$ .....	$2p_2 - ms$ }
	$2p_3 - ms$ }

$$1\Pi_1 = 30113 \cdot 5; 1\Pi_2 = 40138 \cdot 3; 1\Pi_3 = 44768 \cdot 9; 1\Pi_4 = 46536 \cdot 2.$$

$m$ .	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	$m\Sigma$ .
1	12070·23 5460·74 (10) 4358·34 (10) 4046·56 (10)	8282·7 18307·5 22938·1 24705·4	10024·8 4630·6 1767·3	21830·8 21830·8 21830·8 21830·8
2	5025·56 (3) 3341·48 (6) 2893·60 (5) 2752·78 (4)	19892·7 29918·3 34549·1 36316·4	10025·6 4630·8 1767·3	10220·8 10220·0 10219·8 10219·8
3	4140·08 (1) 2925·41 (4) 2576·29 (3) 2464·06 (2)	24147·9 34173·4 38804·1 40571·5	10025·5 4630·7 1767·4	5965·6 5964·9 5964·8 5964·7
4	3815·84 (1) 2759·70 (3) 2446·90 (2) 2345·43 (1)	26199·3 36225·3 40856·1 42623·5	10026·0 4630·8 1767·4	3914·2 3913·0 3912·8 3912·7
5	— 2674·99 (2) 2379·99 (1) —	— 37372·5 42004·6 —	4632·1	— 2765·8 2764·3 —
6	— 2625·24 (2) 2340·60 (1) —	— 38080·7 42711·5 —	4630·8	— 2057·6 2057·4 —
2nd component only.				
7	2593·41 (1)	38548·0		1590·3
8	2571·75 (1)*	38872·7		1265·6
9	2556·30 (1)*	39107·6		1030·7
10	2544·87 (1)*	39283·2		855·1
11	—†	—		—
12	2529·53 (1)*	39521·5		616·8
13	2524·11 (1)*	39606·3		532·0
14	2519·79 (0)*	39674·2		464·1
15	2516·32 (0)*	39728·9		409·4

\* Newly-measured lines.

† Probably obscured by 2536·52.

## Diffuse Quadruplets.

Current Designation.		
$1\Pi_1 - m\Delta'''$	$2P - mD$	- Diffuse Singlets.
$1\Pi_1 - m\Delta''$	$2P - md''$	} - Combination.
$1\Pi_1 - m\Delta'$	$2P - md'$	
$1\Pi_2 - m\Delta_1$	—	
$1\Pi_2 - m\Delta'''$	$2p_1 - mD$	- Combination.
$1\Pi_2 - m\Delta''$	$2p_1 - md''$	} - Diffuse Triplets.*
$1\Pi_2 - m\Delta'$	$2p_1 - md'$	
$1\Pi_2 - m\Delta$	$2p_1 - md$	
$1\Pi_2 - m\Delta_2$	—	
$1\Pi_3 - m\Delta'''$	$2p_2 - mD$	- Combination.
$1\Pi_3 - m\Delta''$	$2p_2 - md''$	} - Diffuse Triplets.*
$1\Pi_3 - m\Delta'$	$2p_2 - md'$	
$1\Pi_4 - m\Delta'''$	$2p_3 - mD$	- Combination.
$1\Pi_4 - m\Delta''$	$2p_3 - md''$	- Diffuse Triplets.*

$$1\Pi_1 = 30113 \cdot 5; 1\Pi_2 = 40138 \cdot 3; 1\Pi_3 = 44768 \cdot 9; 1\Pi_4 = 46536 \cdot 2.$$

$m$ .	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	$m\Delta$ , etc.
2	5790.66 (10r)	17264.5	2.9	12849.0
	5789.69 (2)	17267.4	60.1	12846.1
	5769.60 (10r)	17327.5		12786.0
			10025.7	
	3663.28 (5)	27290.2		12848.1
	3662.88 (4r)	27293.2	3.0	12845.1
	3654.83 (6)	27353.3	60.1	12785.0
	3650.15 (10)	27388.4	35.1	12749.9
			4630.8	
	3131.84 (7)	31921.0	2.9	12847.9
	3131.55 (7)	31923.9	60.1	12845.0
	3125.66 (8)	31984.0		12784.9
			1767.5	
	2967.52 (1)	33688.5	2.7	12847.7
	2967.28 (5)	33691.2		12845.0
3	4347.50 (6n)	22995.3	20.4	7118.2
	4348.64 (2)	23015.7	23.4	7097.8
	4339.23 (4)	23039.1		7074.4
			10025.9	
	3027.48 (2)	33021.2	20.4	7117.1
	3025.62 (2)	33041.6	23.4	7096.7
	3023.47 (4)	33065.0	21.6	7073.3
	3021.50 (5)	33086.6		7051.7
			4630.8	
	2655.13 (4)	37652.0	20.5	7116.9
	2653.68 (4)	37672.5	23.3	7096.4
	2652.04 (5)	37695.8		7073.1
			1767.3	
	—	—†		—
	2534.77 (4)	39439.8		7096.4
4	3906.40 (4n)	25591.8	18.1	4521.7
	3903.64 (2)	25609.9	11.4	4503.6
	3901.90 (2n)	25621.3		4492.2
			10025.1	

## Diffuse Quadruplets—(contd.)

<i>m.</i>	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	<i>m</i> $\Delta$ .
4	2810·51 (0)‡	35570·5	46·4	4567·8
	2806·84 (1)	35616·9	18·0	4521·4
	2805·42 (1)	35634·9	12·2	4503·4
	2804·46 (2)	35647·1	12·5	4491·2
	2803·48 (4)§	35659·6	28·8	4478·7
	2801·22 (0)‡	35688·4	4631·7	4449·9
	2483·83 (2)	40248·6	18·0	4520·3
	2482·72 (3)	40266·6	11·5	4502·3
	2482·01 (4)	40278·1	1765·2	4490·8
	2379·46	42013·8	20·0	4522·4
	2378·34 (3)	42033·8		4502·4
	3704·22 (1)	26988·6	13·7	3124·9
	3702·36 (1)	27002·3	6·5	3111·2
	3701·44 (1)	27008·8	10025·0	3104·7
5	2703·50 (0)‡	36978·3	35·3	3160·0
	2700·92 (1)	37013·6	19·5	3124·7
	2699·50 (1 <sub>n</sub> )	37033·1	8·9	3105·2
	2698·85 (3 <sub>n</sub> )	37042·0	21·5	3096·3
	2697·29 (1)	37063·5	4631·8	3074·8
	2400·52 (0)	41645·4	13·5	3123·5
	2399·74 (2)	41658·9	6·3	3110·0
	2399·38 (3)	41665·2	1767·0	3103·7
	2302·09 (2 <sub>n</sub> )	43425·9		3110·3
	3592·97 (1)	27824·4	11·5	2289·1
	3591·48 (1)	27835·9	4·1	2277·6
	3590·95 (1)	27840·0	10027·4	2273·5
	2642·48 (0)‡	37832·2	19·6	2306·1
	2641·11 (1)‡	37851·8		2286·5
6	2639·93 (3 <sub>n</sub> )	37868·7		2269·6
	2638·85 (1)‡	37884·2	4627·1	2254·1
	2358·48 (1 <sub>n</sub> )	42495·8	1761·0	2273·1
	2258·87 (1)	44256·8		2279·4
	3524·27 (2)	28366·7		1746·8
	3523·00 (1)	28377·2	10026·9	1736·3
	2604·73 (0)‡	38380·5	13·1	1757·8
	2603·84 (1)‡	38393·6		1744·7
	2603·15 (2 <sub>n</sub> )	38403·8	11·3	1734·5
	2602·38 (0)‡	38415·1	4625·7	1723·2
	2323·30 (1 <sub>n</sub> )	43029·5		1739·4
	—	—		—
	—	—		—
	—	—		—
7	—	—		—
	—	—		—
	—	—		—
	—	—		—

First two components only.

## Diffuse Quadruplets—(contd.)

<i>m.</i>	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	$m\Delta$ , etc.
8	3478.98 (1)	28736.4	10.2	1377.1
	—	—		—
	3477.85 (1)	28745.5		1368.0
	2579.58 (0)†	38754.6		1383.7
	2578.91 (0)†	38764.8		1373.5
	—	—		—
	2578.44 (1*)†	38771.9		1366.4
9	3447.22 (1)	29001.0		1112.5
	—	—		—
	—	—		—
	2562.02 (0)†	39020.3		1118.0
	—	—		—
	—	—		—
	2561.18 (1*)†	39033.1		1105.2
1Π <sub>2</sub> — <i>m</i> Δ and satellite only.				
10	2549.24 (0)†	39215.8		922.5
	2548.55 (1*)†	39226.6		911.7
11	2539.00 (1*)†	39374.1		764.2
12	2531.69 (1*)†	39487.8		650.5
13	2525.84 (1*)†	39579.2		559.1
14	2521.23 (1*)†	39651.5		486.8
15	2517.45 (1*)†	39711.1		427.2
16	2514.26 (1*)†	39761.4		376.9
17	2511.64 (1*)†	39802.9		335.4
18	2509.47 (0*)†	39837.3		301.0
19	2507.47 (0*)†	39869.1		269.2
20	2505.87 (0*)†	39894.5		243.8

\* Wiedmann's diffuse triplet series, referred to in the paper, is, in the present notation—

1Π <sub>2</sub> —mΔ'''	1Π <sub>2</sub> —mΔ'''	1Π <sub>4</sub> —mΔ'''
1Π <sub>2</sub> —mΔ''	1Π <sub>3</sub> —mΔ''	1Π <sub>4</sub> —mΔ''
1Π <sub>2</sub> —mΔ'	1Π <sub>3</sub> —mΔ'	

As stated, this leaves the strong series, 1Π<sub>2</sub>—mΔ, unaccounted for.

† Frequency difference relations require  $\nu = 39419.3$ , i.e.,  $\lambda = 2536.09$ . This line would be weak, and is probably obscured by the strong line 2536.52.

‡ Newly-measured lines. See note in paper, added July 28, 1921.

§ This line has another newly-measured satellite, 2802.76 (1).

|| This line, and the corresponding lines of succeeding members of the series, represent the unresolved pairs, 1Π<sub>2</sub>—mΔ', 1Π<sub>2</sub>—mΔ.

Fundamental Quadruplets.

	Current Designation.
$2\Delta - m\Phi$ .....	$3d - mf$ } Fundamental Triplets.
$2\Delta' - m\Phi$ .....	$3d' - mf$ }
$2\Delta'' - m\Phi$ .....	—
$2\Delta''' - m\Phi$ .....	$3d'' - mf$ } Fundamental Triplets.
$2\Delta = 12749 \cdot 9$ ; $2\Delta' = 12785 \cdot 3$ ; $2\Delta'' = 12845 \cdot 3$ ; $2\Delta''' = 12848 \cdot 1$ .	

$m$ .	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	$m\Phi$ .
3	17193 (1)	5814 · 8	28 · 7	6935 · 1
	17108 · 51 (1)	5843 · 5	58 · 5	6941 · 8
	16938 · 86 (1)	5902 · 0	7 · 2	6943 · 3
	16918 · 32 (2)	5909 · 2		6938 · 9
4	12020 · 20 (1)	8317 · 2		4432 · 7
	—	—		—
	11886 · 64 (1)*	8410 · 6		$\begin{cases} 4434 \cdot 7 \\ 4437 \cdot 5 \end{cases}$

\* Stated by Paschen to be a double line, with wave-length separation of  $10 \text{ \AA}$ .U.

Quadruplet Combination Series.

	Current Designation.
$1\Pi_1 - m\Phi$ .....	—
$1\Pi_2 - m\Phi$ .....	$2p_1 - mf$ }
$1\Pi_3 - m\Phi$ .....	$2p_2 - mf$ } — Combination.
$1\Pi_4 - m\Phi$ .....	$2p_3 - mf$ }
$1\Pi_1 = 30113 \cdot 5$ ; $1\Pi_2 = 40138 \cdot 3$ ; $1\Pi_3 = 44768 \cdot 9$ ; $1\Pi_4 = 46536 \cdot 2$ .	

$m$ .	$\lambda$ and intensity.	$\nu$ .	$\Delta\nu$ .	$\nu$ (calc.).†	$\Delta\nu$ (calc.).
3	4313 · 3 (1v)	23177 · 7		23173 · 7	
	3011 · 05 (1u)	33201 · 4	10023 · 7	33193 · 5	10024 · 8
	2642 · 60 (6v)*	37830 · 5	4629 · 1	37829 · 1	4630 · 6
	2524 · 71 (1r)	39596 · 9	1766 · 4	39596 · 4	1767 · 3
4	3893 · 89 (1u)	25674 · 2		25679 · 1	
	2799 · 83 (2)	35706 · 1	10031 · 9	35703 · 9	10024 · 8
	2478 · 66 (1)	40332 · 6	4626 · 5	40334 · 5	4630 · 6
	2374 · 02 (2u)	42110 · 2	1777 · 6	42101 · 8	1767 · 3

\* Intensity given is by Kayser and Runge. Stiles gives it as (1). Intensity is probably affected by neighbourhood of  $1\Pi_2 - 6\Delta_1$ .

† The discrepancies between observed and calculated wave-numbers of some of these lines may partly be attributed to uncertainty in the values of  $m\Phi$ . The fundamental series is well in the infra-red, and, as shown above, the values of  $m\Phi$  from different components show rather large variations. The mean values of  $m\Phi$  have been adopted in this column.



## Singlet System.

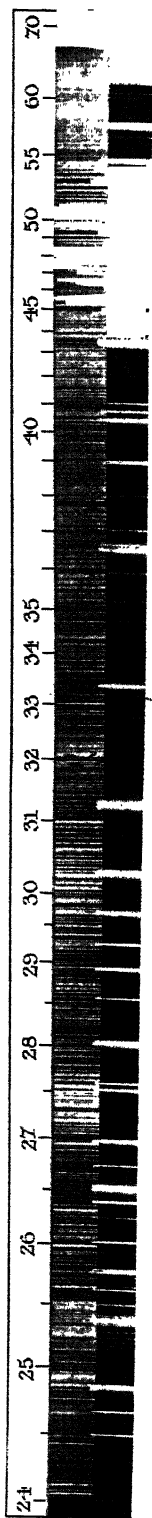
	m.	$\lambda$ and intensity.	$\nu$ .	mP.	Current Designation.
I. Principal Singlets— $1\Pi_3 - mP$ ..... $1\Pi_3 = 44768 \cdot 9$	1 2 3 4 5	—2536·52 (10R) 4077·83 (7r) 2866·94 (1) 2568·90 (1) 2441·08 (1)*	—39412·6 24515·9 34092·4 38691·7 40954·4	$\left. \begin{array}{l} 84181 \cdot 5 \\ 20253 \cdot 0 \\ 9776 \cdot 5 \\ 5777 \cdot 2 \\ 3814 \cdot 5 \end{array} \right\}$	$2p_2 - mS - \text{Combination.}$
II. Diffuse Singlets— $1P - m\Pi_1$ ..... $1P = 84181 \cdot 5$ .	1 2	1849·67 1402·72 (p)†	54065·7 71290·0	$m\Pi_1$ $\left. \begin{array}{l} 30115 \cdot 8 \\ 12890 \cdot 9 \text{ (?) } \end{array} \right\}$	$1 \cdot 5 S - mP - \text{Principal Singlets (1).}$
III. Sharp Singlets— $1P - m\Pi_3$ ..... $1P = 84181 \cdot 5$ .	1 2	2536·52 (10R) 1435·63	39412·6 69655·8	$m\Pi_3$ $\left. \begin{array}{l} 44768 \cdot 9 \\ 14526 \cdot 7 \end{array} \right\}$	$1 \cdot 5 S - mp_2 - \text{Combination.}$
IV. Combination Series— $1\Pi_1 - mP$ ..... $1\Pi_1 = 30113 \cdot 5$ .	1 2 3 4 5	—1849·67 10139·67 4916·04 (4r) 4108·08 (2n) 3801·67 (2)	—54065·7 9859·7 20335·9 24335·4 26296·8	$\nu$ (calc.) —54068·0 $\left. \begin{array}{l} 9860 \cdot 5 \\ 20837 \cdot 0 \\ 24336 \cdot 3 \\ 26299 \cdot 0 \end{array} \right\}$	$2P - mS - \text{Sharp Singlets.}$
V. Combination Series— $2P - m\Pi_1$ ..... $2P = 20253 \cdot 0$ .	1 2 3 4 5 6 7 8 9 10 11	—10139·67 $\frac{p}{p}$ 6716·45 (5) 6234·35 (8) 5803·55 (4r)† 5549·28 (3r) 5393·50 (2) 5290·1 (2) 5218·9 (2) 5165·8 (1) 5128·9 (1)	—9859·7 $\frac{p}{p}$ 14884·8 16085·8 17226·1 18015·4 18535·8 18897·9 19155·7 19852·2 19492·0	$\left. \begin{array}{l} -9860 \cdot 5 \\ \frac{p}{p} \\ 14884 \cdot 1 \\ 16086 \cdot 7 \\ 17225 \cdot 8 \\ 18015 \cdot 3 \\ 18536 \cdot 9 \\ 18898 \cdot 7 \\ 19153 \cdot 5 \\ - \\ - \end{array} \right\}$	$2 \cdot 5 S - mP - \text{Principal Singlets (2).}$

\* Newly-measured line.

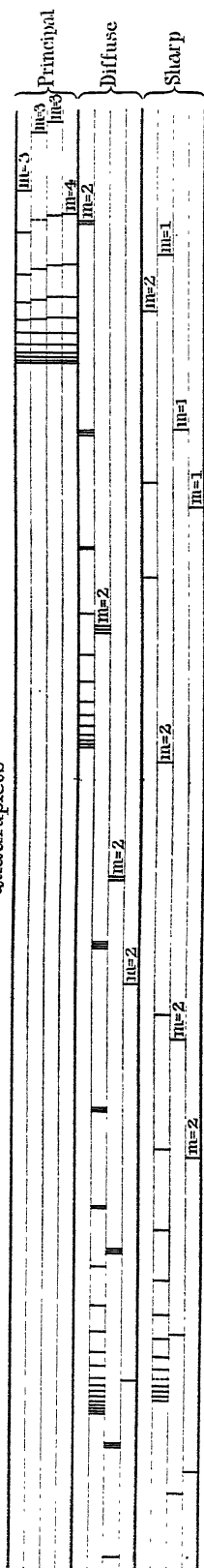
† Paschen so classifies this line by assuming  $\lambda 13570 \cdot 68$  to be the line  $2P - 2\Pi_1$ . He questions the truth of this, however, and the value of  $2\Pi_1$ , which it gives leads to a line for  $1\Sigma - 2\Pi_1$  which has not been observed, and which is unlikely in view of its closeness to  $\lambda 11287 \cdot 16$  ( $1\Sigma - 2\Pi_1$ ). It is probable, therefore, that  $\lambda 1402 \cdot 72$  and  $\lambda 13570 \cdot 68$  do not take part in any of the series given in this paper, but are combination lines, associated by the fact that their wave-number difference is equal to  $1P - 2P$ . They would form, for instance, the first two members of a series  $91545 - mP$ . The third member of such a series ( $\lambda = 1293$ ) would lie outside the present boundary of investigation in the ultra-violet. The limit of the series, however, does not appear to be derivable from the terms of existing series.

‡ See footnote (†) on p. 174.

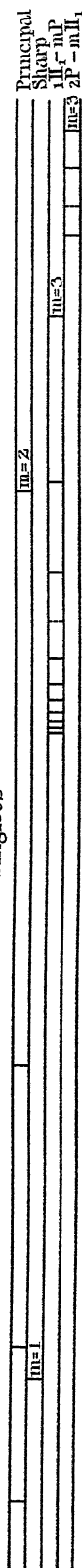




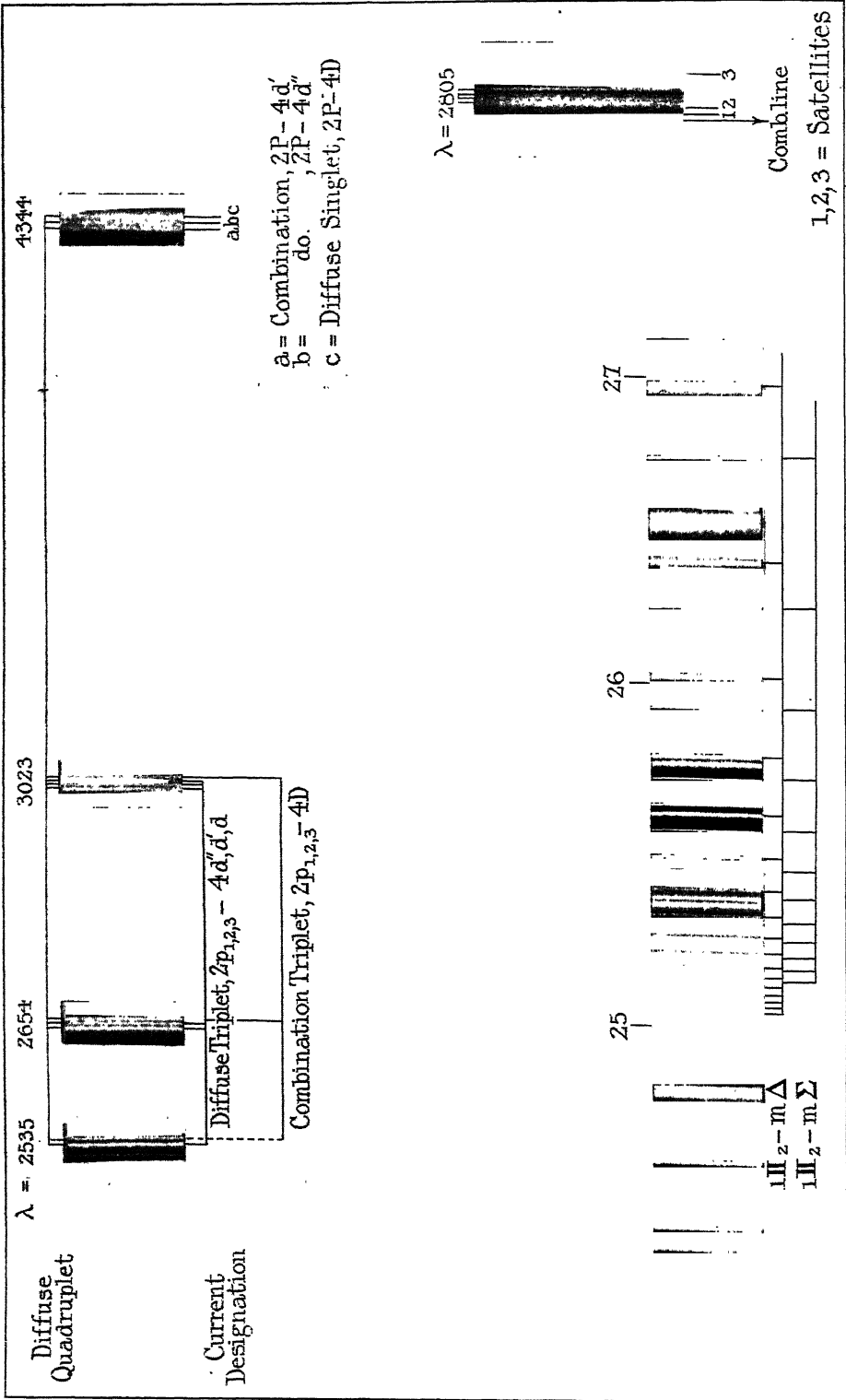
Quadruplets



Singlets







Combination Lines.

$\lambda$ and intensity.	$\nu$ .	$\nu$ (calc.)	Formula.	Current designation.
17071.54 (2)	5856.2	5856.1	$2\Pi_2 - 3\Delta'''$	$3p_1 - 4D$
3680.01 (5)	27166.1	27164.8	$1\Pi_2 - 2\Pi_2$	$2p_1 - 3p_1$
3050.46 (1 <sub>n</sub> )*	32772.5	32780.5	$1\Pi_2 - 3\Pi_2$	$2p_1 - 4p_1$
3085.29 (1 <sub>n</sub> )	32402.5	32403.7	$1\Pi_2 - 3\Pi_4$	$2p_1 - 4p_2$
3144.48 (2 <sub>r</sub> )	31792.6	31795.4	$1\Pi_3 - 2\Pi_2$	$2p_1 - 3p_1$
2672.67 (1 <sub>n</sub> )*	37404.8	37411.1	$1\Pi_3 - 3\Pi_2$	$2p_2 - 4p_1$
3305.09 (1 <sub>r</sub> )	30247.7	30249.8	$1\Pi_3 - 2\Pi_3$	$2p_2 - 3p_2$
3135.76 (2 <sub>n</sub> )*	31881.0	31871.6	$1\Pi_4 - 2\Pi_4$	$2p_3 - 3p_3$
36258 (2)	2757.3	2753.4	$2\Pi_2 - 2\Sigma$	$3p_1 - 3.5s$
23263 (3)	4297.6	4299.0	$2\Pi_3 - 2\Sigma$	$3p_2 - 3.5s$
22489 (3)	4445.4	4444.5	$2\Pi_4 - 2\Sigma$	$3p_3 - 3.5s$

\* These lines are given as combinations by Paschen ('Ann. d. Phys.,' vol. 35). The somewhat large differences between observed and calculated wave-numbers cast some doubt on the identification.

Description of Plates 4 and 5.

4. In the analysis of the spectrum, each series formed of corresponding components of a quadruplet series is given a separate row. The value of  $m$  is indicated for the first line in each row. A complete quadruplet is composed of four components, having the same value of  $m$ , one taken from each row of the space allotted to the series to which it belongs. In the diffuse series, the four components contain, respectively, 3, 4, 3, 2 lines, but they are not, in most cases, completely resolved in the reproduction. (In printing, the wavelength scale has been displaced very slightly to the right.)

5. This plate shows separate portions of the spectrum appearing in Plate 4, as described in the paper. The distances between the components of the second diffuse quadruplet are not on the same scale as the intervals between the lines forming each component. The component of the third diffuse quadruplet, with satellites, which is shown separately, is on a larger scale than the other photographs on the plate.

In conclusion, I wish to express my thanks to Prof. A. Fowler, F.R.S., for constant advice and help, both direct and indirect, in the work leading up to this paper, and to Mr. F. S. Phillips, B.Sc., for permission to reproduce the photograph used in the plates.

*The Spectrum of Ionised Potassium.*

By J. C. McLENNAN, F.R.S., Professor of Physics, University of Toronto.

(Received June 29, 1921.)

[PLATE 6.]

In 1904 Eder and Valenta\* found that potassium, under the excitation of a sharp spark discharge, could be made to emit, in addition to the ordinary arc series spectrum, a new one, which was rich in wave-lengths and which extended into the ultra-violet. In 1907, Goldstein† found this spectrum could, when special experimental arrangements were adopted, be obtained pure and unmixed with any of the wave-lengths of the arc spectrum. To it he gave the name the "ground spectrum" of potassium.

In his paper Goldstein gives the values of the wave-lengths of a few of the constituents of this spectrum, but as the discharge tubes used by him were made of glass, his list of wave-lengths did not extend beyond the visible.

In 1909 a further study of this "ground spectrum" was made by Schillinger‡, and the wave-lengths were determined by him not only in the visible region but also in the violet and the ultra-violet region as far as  $\lambda = 2144.6 \text{ \AA.U.}$

In 1915 some observations were also made by Edgar H. Nelthorpe§ on the "ground spectra" of the alkali and alkaline earth metals, in which the wave-lengths for potassium were measured from  $\lambda = 6307 \text{ \AA.U.}$  to  $\lambda = 3897.9 \text{ \AA.U.}$

Recently Sommerfeld|| has revived interest in this spectrum through his pointing out that the configurations of the extra-nuclear electron systems of the positive ions of the alkali metals are, on the basis of the views which are commonly held at present regarding the structure of atoms, likely to be identical with the configurations of the extra-nuclear electron systems of the atoms of the rare gases. This will be made evident by the representations of atomic structure given in fig. 1.

From these it will be seen that the number of the extra nuclear electrons associated with the atoms of the various elements cited is determined by the atomic numbers of these elements. Moreover, the atoms of the alkali metals are similar in that they all have but one electron in their outside ring.

\* Eder and Valenta, 'Denkschr. Wien. Akad.,' vol. 61, p. 347 (1894).

† Goldstein, 'Verh. d. Deut. Phys. Ges.,' vol. 9, p. 321 (1907).

‡ Schillinger, 'Wien. Ber.,' vol. 118, IIA, p. 266 (1909).

§ Nelthorpe, 'Ast. Phys. Jour.,' No. 41, p. 16 (1915).

|| Sommerfeld, 'Atombau und Spektrallinien,' p. 296.

Their similarity in this respect is paralleled by the fact that in the arc spectra of the alkali elements the wave-lengths can be grouped into doublet

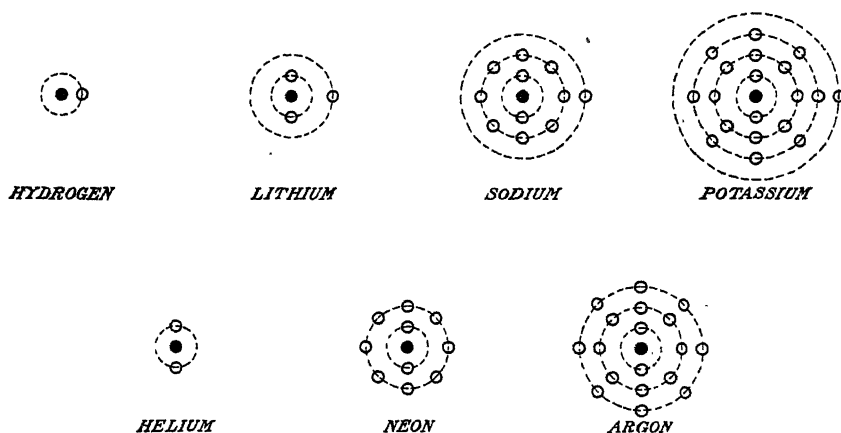


FIG. 1.

series which are the same in number and the same in type for all the elements in the alkali group. Going one step further, Sommerfeld has emphasised the view that these doublet series of wave-lengths in the spectra of the alkali elements have their origin in the outside ring electron of the atoms of the respective elements.

When an element of the alkali group is subjected to spark excitation, it is assumed that the violence of the disturbance to which the atoms are subjected is so great that the outer electron is removed entirely from these atoms and that the radiations which are emitted by them under these circumstances must have their origin in the electrons still remaining. Such radiations would constitute the so-called enhanced spectra. Taking potassium, for example, it will be seen that when the outer electrons are removed from the atoms of this element, the configuration of the electrons still remaining is identical with the extra-nuclear electron system of an ordinary atom of argon. It follows, then, that the enhanced spectrum of potassium should be identical in type with the ordinary arc spectrum of argon.\* The only difference between the two spectra would be that in the case of potassium, where the nuclear charge is one unit higher than that of argon, the enhanced

\* [Footnote added September 20, 1921.—It may be that the ordinary spectra of argon can be obtained as well from an electric discharge in the gases and vapours obtainable from heated potassium. This element and rubidium are known to be radioactive. They emit beta-rays and possibly, too, alpha-rays. The emission of such radiations would indicate the possibility of potassium being transmuted into argon and of rubidium into krypton.]



spectrum might be expected to appear farther down in the violet or ultra-violet region.

Now argon is known to be capable of emitting two types of spectrum, the one known as the red spectrum, which is produced under conditions of moderate excitation, and the other the blue spectrum, emitted when violent or intense stimulation is used. From this it follows that it should be possible to cause the atom of potassium to emit three definite and distinct types of spectrum. The first would be the ordinary arc spectrum of the element—the spectrum which constitutes the doublet system; the second would correspond with and be similar to the red spectrum of argon; and the third would represent the blue spectrum of this element. The first would be the result of moderate excitation, the second of more or less intense excitation, and the third would probably be obtained when the stimulation was extremely violent.

From the considerations presented above it seems clear that we have in the “ground spectrum” of potassium, discovered by Eder and Valenta, the enhanced spectrum of that element. Moreover, if the views put forward by Sommerfeld be correct, it would follow that the enhanced spectrum should possess characteristics identical with those of the red spectrum of argon, and possibly, too, if the excitation used were sufficiently intense, of the blue spectrum.

The present investigation was begun with the object of putting these views to the test. It was intended to do so by calculating the ratios of the frequencies of the wave-lengths in the red and blue spectra of argon and by comparing them with the ratios of the frequencies of the wave-lengths of the enhanced spectrum of potassium, using Schillinger's results for the calculation of the latter. But prior to this enquiry, some observations were made on the enhanced spectrum of potassium, in the course of which it was found that a great many wave-lengths came out on the plates which had not been observed by Schillinger. The original programme was therefore deferred for a time, and an effort was made to obtain as complete a record as possible of the wave-lengths of the radiations emitted by potassium under intense excitation. The results of this part of the investigation are given below.

### 1. *Mode of Excitation.*

Various types of arcs in potassium vapour with high potential differences applied to the electrodes were tested, but with none of them was the enhanced spectrum far down in the ultra-violet region obtained. The spark discharge in air proved equally unsatisfactory in this respect.

When, however, a very powerful electrodeless discharge was used with potassium vapour of low density, the enhanced spectrum came out strongly

and clearly. In obtaining the electrodeless discharge, a 12-inch induction coil was used, with its secondary joined in parallel with two sets of four Leyden jars, each having a volume of about one gallon.

The coil was operated with a Wehnelt interrupter joined to the 110 D.C. mains. Pyrex glass bulbs about 9 cm. in diameter were used for holding the potassium, and these were provided with a side tube closed by a fluorite window when the ultra-violet spectrum was being photographed with quartz and fluorite spectrographs.

Prior to introducing the potassium into the bulbs the latter were thoroughly exhausted, and during the exhaustion they were heated to about 400° C. in order to drive out any gases occluded in their walls. The potassium was distilled into the bulbs from a side tube which was sealed off after sufficient potassium had been introduced. In working with a vacuum grating spectrograph, the side tube of the pyrex glass bulbs was used without the fluorite

Table I.—List of Wave-lengths obtained by Author in region between  $\lambda = 6950 \text{ \AA.U.}$  and  $\lambda = 3489 \text{ \AA.U.}$ , with electrodeless discharge in potassium vapour, in addition to those obtained by Schillinger\* for the same spectral region with the spark discharge.

Intensity.	Wave-length.	Remarks.
	$\lambda \text{ (\AA.U.)}$	
3	6050	
2	5730	
1	4958	Ramage,† 4957; Kayser and Runge‡, 4956·8.
3	4863	Liveing and Dewar,§ 4863·8; Ramage, 4862.
1	4805	Liveing and Dewar, 4803·8.
1	4790	Liveing and Dewar, 4788·8.
1	4769	Ramage, 4767.
1	4760	Liveing and Dewar, 4759·8.
1	4744	
1	4720	
1	4688	
1	4648	Saunders, 4642·5.
2	4454	
2	4365	
1	4103	
3	3660	
4	3660	
1	3590	
1	3583	
1	3572	
1	3489	

\* Schillinger, 'Wien. Ber.,' vol. 118, IIA, p. 266 (1909)

† Ramage, 'Roy. Soc. Proc.,' vol. 70, p. 304 (1902).

‡ Kayser and Runge, 'Spectroscopie,' vol. 5, p. 635 (1910).

§ Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 29, p. 398 (1879).

|| Saunders, 'Ast. Phys. Jour.,' vol. 20, p. 188 (1904).

Table II.—Ultra-Violet Spectrum of Potassium (Electrodeless Discharge).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	$\lambda$ (Å.U.).		$\lambda$ (Å.U.).
6	3345·8	5	3345·8
3	3336·7		
3	3324·65		
		4	3322·46
5	3312·7	4	3312·77
3	3303·5		
5	3292·25	3	3291·07
3	3279·1	3	3278·84
3	3262·5	2	3262·02
3	3257·4		
3	3244·5		
		2	3241·14
1	3223·7	1	3224·66
0	3220·0	2	3220·93
		1	3218·87
		1	3217·54
0	3213·0		
		4	3209·45
4	3205·6		
		3	3202·09
5	3189·0	2	3190·55
		2	3188·04
2	3174·0		
4	3171·9	1	3170·02
3	3159·4		
		1	3157·62
2	3148·6		
4	3130·6	2	3129·52
		4	3105·43
6	3104·3		
		1	3103·05
2	3076·95		
		1	3074·55
5	3062·15	5	3062·56
0	3057·0	2	3056·96
2	3052·85	3	3052·17
2	3048·6		
3	3031·6	1	3030·79
3	3024·8	2	3023·56
3	2993·4	3	2992·47
2	2985·9	1	2986·05
1	2966·9		
		1	2963·37
1	2955·8		
2	2939·5	1	2938·55
1	2926·8		
2	2904·9		
2	2855·7	1	2854·06
3	2836·2		
		1	2833·25
2	2825·7		
3	2819·6	1	2819·24
5	2803·8		
		1	2780·2
1	2778·0		
1	2768·1		
2	2742·8	1	2743·5

Table II.—(contd.).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	$\lambda$ (Å.U.).		$\lambda$ (Å.U.).
4	2735·6	1	2736·1
1	2732·0		
3	2689·1	1	2690·5
3	2661·1		
1	2655·8	1	2635·7
4	2633·9		
0	2630·0	1	2614·2
2	2612·9		
1	2569·8	1	2549·6
2	2559·2	1	2538·7
4	2549·6		
3	2536·0		
2	2502·4	1	2474·3
3	2475·6		
3	2470·4		
2	2451·25	1	2440·7
4	2446·0		
2	2440·9		
4	2436·6		
3	2410·4		
3	2402·0		
3	2393·4	1	2379·6
4	2376·3		
5	2370·25		
2	2365·8		
7	2362·6	1	2358·9
3	2351·9	1	2350·3
4	2348·3		
3	2343·2	1	2343·2
3	2340·15		
0	2335·0		
0	2332·0		
2	2328·27	1	2328·0
3	2324·33		
5	2319·15		
4	2315·22		
0	2312·0	1	2311·7
0	2309·0		
3	2306·58		
1	2304·0		
3	2300·9		
2	2295·16		
0	2290·0		
2	2284·32		
3	2280·05		
0	2278·0	1	2274·2
5	2270·9		
5	2265·04	1	2262·2
3	2262·0	1	2261·8
5	2260·32	1	2260·7
		1	2257·9
3	2255·29	1	2255·0

Table II.—(contd.).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	$\lambda$ (Å.U.).		$\lambda$ (Å.U.).
2	2253·0		
5	2250·92		
0	2248·0	1	2248·2
2	2246·82		
2	2243·0		
6	2240·89		
0	2237·0		
2	2231·87		
2	2226·0		
5	2221·58		
3	2217·23		
4	2213·1		
4	2210·53		
4	2206·28	1	2205·2
0	2203·0	1	2203·7
2	2200·89		
3	2194·89	1	2196·8
6	2190·0		
6	2186·93		
1	2182·4		
3	2177·92		
3	2175·12		
2	2171·03		
1	2163·31		
0	2159·0		
4	2155·3		
0	2152·0		
3	2149·42		
7	2143·9	1	2144·6
1	2141·0		
1	2140·49		
5	2137·56		
3	2132·8		
4	2130·75		
4	2128·9		
4	2127·25		
4	2122·0		
3	2114·2		
3	2110·05		
1	2105·45		
0	2102·0		
1	2101·05		
3	2100·0		
3	2097·65		
2	2093·8		
6	2089·8		
4	2085·2		
3	2082·1		
10	2077·9		
0	2071·0		
2	2070·0		
1	2067·2		
2	2062·05		
4	2054·9		
1	2053·1		
2	2049·8		
1	2045·7		

Table II.—(contd.).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	$\lambda$ (Å.U.).		$\lambda$ (Å.U.).
1	2043·1		
6	2036·9		
1	2027·8		
1	2019·6		
2	2010·7		
2	2006·8		
2	1999·2		
4	1995·1		
3	1981·6		
3	1976·4		
1	1974·7		
2	1965·1		
2	1960·2		
2	1952·6		
5	1944·6		
1	1940·9		
3	1933·5		
1	1930·8		
1	1926·3		
2	1923·8		
2	1921·4		
1	1908·4		
1	1905·9		
1	1904·5		
2	1902·8		
1	1897·8		
2	1894·8		
1	1892·5		
1	1891·7		
2	1890·6		
1	1873·9		
2	1873·3		

window and was attached directly to the spectrograph so as to permit the slit of the latter to be strongly and directly illuminated by the radiation emitted by the discharge in the bulb.

## 2. Results.

Reproductions of the photographs of the spectra obtained with small and large quartz spectrographs of the Hilger type are shown in Plate 6, and the mean values of the wave-lengths obtained from measurements on a number of photographic plates are given in Tables I and II. The values given in Table I are to be considered as correct to one-half an Ångström unit.

From the Tables it will be seen that over 150 wave-lengths were recorded in addition to those previously observed by Schillinger.

In photographing the spectrum with a vacuum grating spectrograph wave-lengths were recorded at  $\lambda = 1742\cdot2$ ,  $1493\cdot4$ ,  $1395\cdot4$ ,  $1199\cdot7$ ,  $1135\cdot0$  and

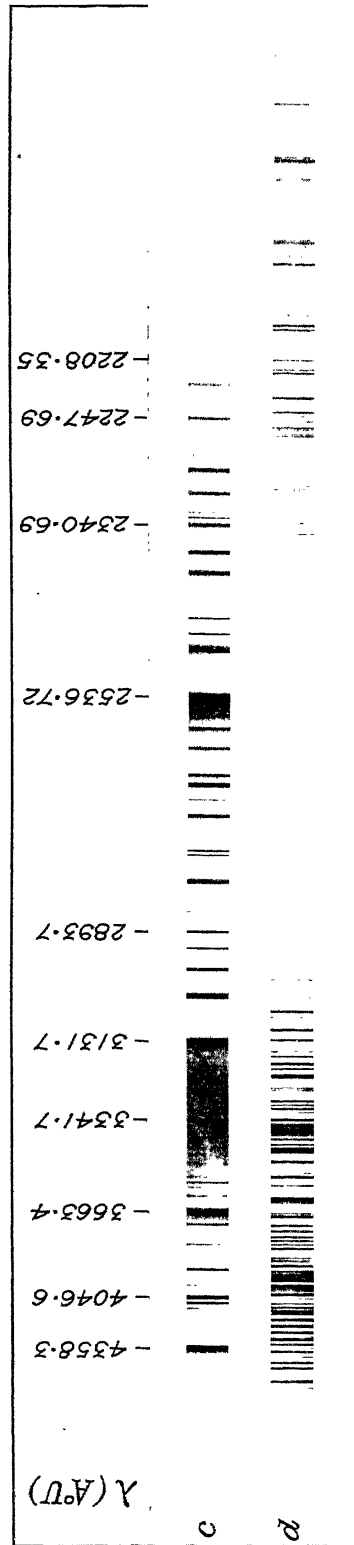
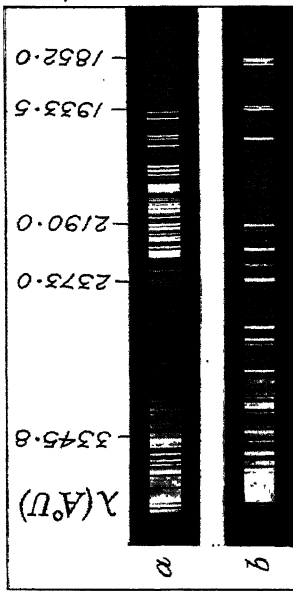
1085.3 Å.U. Of these wave-lengths  $\lambda = 1742.2$  Å.U. may possibly belong to the spectrum of potassium. The remaining five came out with strong intensity on numerous occasions when photographing the spectrum of helium. Some difficulty has been experienced in fixing the identity of these wave-lengths, though there are indications that some, at least, of them may have originated in the atoms of mercury through a slight diffusion of the vapour of this element from a Langmuir condensation pump which was used in conjunction with a set of Trimount oil pumps to evacuate the spectrographs.

From the reproductions of the enhanced spectrum of potassium shown in the Plate it will be seen that the wave-lengths, from the point of view of numbers and intensity, fall roughly into two divisions with a certain amount of overlapping. In the one division the "optical" or "spectral" centre of gravity is approximately at  $\lambda = 3800$  Å.U. and in the other it is in the neighbourhood of  $\lambda = 2100$  Å.U. This suggests that we have here spectra which are analogous to the ordinary and enhanced spectra of argon, the one with its spectral centre of gravity at  $\lambda = 3800$  Å.U., corresponding to the red spectrum of argon, and the other with its spectral centre of gravity at  $\lambda = 2100$  Å.U., corresponding to the blue spectrum of this element.

It is proposed to make an analysis of the frequencies of the wave-lengths recorded in the Tables and of the additional ones given by Schillinger in order to see if this parallelism can be established numerically. If such a numerical parallelism can be established it will constitute a definite confirmation of the view put forward by Sommerfeld.

In concluding, I wish to express my thanks to my assistants, Messrs. P. A. Petrie and P. Blackman, for helping me to take the photographs, and to Mr. Vladimir Lubowich and several of my students, for measuring the plates and checking the results for me.

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*On the Refractive Indices of Mercury and Thallium Vapours.*

By J. C. McLENNAN, F.R.S., Professor of Physics, University of Toronto.

(Received June 29, 1921.)

1. *Introduction.*

Although numerous accurate and extended determinations have been made of the refractive indices of gases which exist as such at ordinary temperatures, few have been made with the vapours of elements or compounds which, at room temperatures, are solids and possess a low equilibrium vapour pressure in that state.

Notable among the latter are the determinations made by Prof. R. W. Wood\* with sodium vapour and those made by Messrs. C. Cuthbertson and E. Parr Metcalfe† with the vapours of sulphur, phosphorus, mercury, zinc, cadmium, selenium, and tellurium. In the work of both of these investigations an interference method was adopted. In Wood's a Michelson interferometer was used and in Cuthbertson and Metcalfe's one of the Jamin type. For the investigation of Cuthbertson and Metcalfe the glass interferometer tubes ordinarily used with Jamin interferometers were wholly unsuitable. These, as is well known, are provided with plane parallel plate glass ends ground in and luted with shellac or a wax having similar properties, and when heated to 300° C. or higher, the shellac chars and the tubes frequently crack, soften, or become distorted. For these reasons Cuthbertson and Metcalfe had recourse to interferometer tubes made of fused silica which were made, with great skill, by Messrs. Heraeus, of Hanau. The ends of the tubes through which the interfering rays passed were plates of quartz ground optically flat, fused into the tubes and again polished. In their manufacture such tubes are, however, difficult to make. Failures are frequent and consequently the tubes are expensive. On this account investigators have been deterred hitherto from studying the refractivities of the vapours of metals and other substances, having moderately high melting points and vapourising temperatures.

A short time ago the writer found that hollow prisms of any angle with optically flat faces, and interferometer tubes with plane parallel end-plates, could be made with ease and at a low cost out of clear fused quartz. These were tried out with mercury vapour and results obtained which showed a

\* Prof. R. W. Wood, 'Phil. Mag.,' September, 1904.

† Messrs. C. Cuthbertson and E. Parr Metcalfe, 'Phil. Trans.,' A, vol. 207, p. 135 (1908).

good agreement with the values recorded by Cuthbertson and Metcalfe for this metal.

As no determinations appeared to have been made with thallium vapour, and as it gave promise of interesting results, an attempt was made to measure the refractive indices of this element for a number of wave-lengths. No practical difficulties were experienced in working with this metal, and, from the success which accompanied the attempt, it would appear that, with the use of the fused quartz apparatus referred to above, the refractive indices of metals having a moderately high melting point can be determined with as much ease as those of an ordinary gas.

## 2. *Fused Silica Prisms and Interferometer Tubes.*

The method followed in making up hollow silica prisms and interferometer tubes was based on the work of Messrs. R. G. Parker and A. J. Dalladay,\* who found that optical parts of silica when placed in contact would fuse together if heated to a temperature somewhat below  $1200^{\circ}\text{C}$ .—the point of devitrification. In applying this principle, however, it was found that unless special precautions were taken it was extremely difficult to attach plane parallel end-plates to interferometer tubes or face plates to prisms, with an oxy-gas or oxy-hydrogen blowpipe, without distorting the plates and without coating the surfaces exposed to the flame with a thin layer of devitrified silica. These difficulties were, however, readily overcome by adopting a procedure first used by Messrs. Gibson and Argo.† Figs. 1 and 2 will serve to illustrate the method adopted.

A tube AB, fig. 1, of clear fused silica from 1.0 to 1.5 cm. in diameter was first of all selected, care being taken to have the bore as uniform as possible.

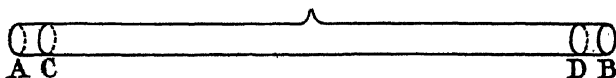


FIG. 1.

Two discs, C and D, were then cut from a plate of clear fused quartz which had been worked optically flat and these were carefully ground to a diameter the same as that of the bore of the interferometer tube. The discs were then inserted in the tubes, as shown in the diagram, at from two to three centimetres from the ends of the tube, and were held at right angles to the axes of the tube by means of two projection lamp carbons with plane ends. The finely pointed flame of an oxy-hydrogen blowpipe was then directed in the plane of the disc against the outside of the tube, until the wall of the latter

\* Parker and Dalladay, 'Chem. News,' December 29, 1916, p. 310.

† Gibson and Argo, 'Jl. Am. Chem. Soc.,' vol. 40, No. 9, p. 1327, September, 1918.

slightly softened. By means of the pointed end of an ordinary file the softened tube wall was then gently pressed against the edge of the disc, when adhesion was readily obtained. To obtain adhesion all round the disc it was only necessary to heat the tube point by point all round its circumference. After this was done, it was generally advisable to rotate the tube slowly for a short time with the line of union just within the pointed end of the flame. By following this method, by which the flame did not come in contact with the discs, it was found that interferometer tubes could be readily, easily and cheaply made, with end plates beautifully clear and without any trace of distortion, except close to the edges.

Fig. 2 will indicate the procedure adopted in making up the hollow prisms. In this case the discs were ground in the shape of ellipses, the dimensions of the latter being determined by the refracting angles selected for the prism and the diameter of the tube used. The procedure followed in effecting union between the edges of the discs and the wall of the tube was precisely the same as that followed in making up the interferometer tubes. After the prism was made, the projecting portions of the main tube were cut off so as not to interfere with the rays entering or leaving the prism.

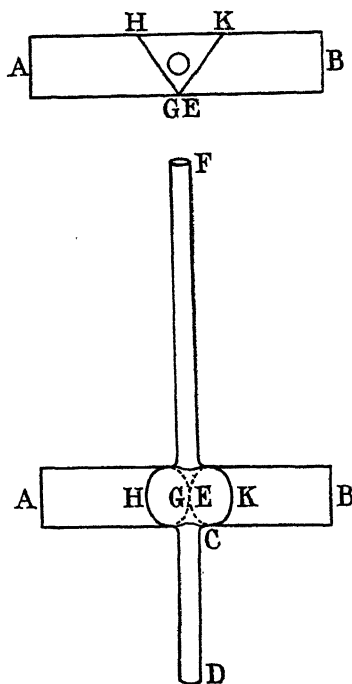


FIG. 2.

### 3. Interferometric Determinations.—Theory.

The theory for the determination of the refractive indices of a vapour by means of the Jamin interferometer is well known, and may be summarised as follows:—

Let  $\rho_1$  be the density of the saturated vapour at temperature  $t_1$ ,

$\rho_2$         "        "        "        "         $t_2$ ,

$\rho_0$  be a selected standard density of the vapour.

Let  $\mu_1, \mu_2, \mu_0$  respectively be the refractive indices of the vapour corresponding to the densities  $\rho_1, \rho_2, \rho_0$  for a selected wave-length.

Let  $\lambda_0$  be the wave-length of the selected light *in vacuo*, and  $\lambda_1, \lambda_2$  the wave-lengths of the same radiation in the vapour at the densities  $\rho_1$  and  $\rho_2$ .

Let  $L$  be the length of the interferometer tube and  $x$  be the number of interference bands which pass a fiducial mark during the evaporation or condensation.

Then  $L = n_1\lambda_1 = n_2\lambda_2$  where  $n_1 - n_2 = x$ ,

$$\lambda_1 = \frac{\lambda_0}{\mu_1}, \quad \lambda_2 = \frac{\lambda_0}{\mu_2},$$

$$\therefore L = \frac{n_1\lambda_0}{\mu_1} = \frac{n_2\lambda_0}{\mu_2} = \frac{n_1 - n_2}{\mu_1 - \mu_2} \lambda_0,$$

$$\therefore \mu_1 - \mu_2 = \frac{x\lambda_0}{L}.$$

But 
$$\frac{\mu_1 - 1}{\rho_1} = \frac{\mu_2 - 1}{\rho_2} = \frac{\mu_0 - 1}{\rho_0} = \frac{\mu_1 - \mu_2}{\rho_1 - \rho_2},$$

$$\therefore \mu_0 - 1 = \frac{x}{\rho_1 - \rho_2} \frac{\lambda_0 \rho_0}{L},$$

from which it follows that  $x/\rho_1 - \rho_2$  should be constant, for any two selected densities of the vapour.

#### 4. *Interferometer Experiments with Mercury Vapour.*

In these experiments the interferometer tubes, one of which contained a quantity of mercury, were enclosed in an electric furnace made of nichrome wire wound on a cylinder of sheet rolled asbestos. This furnace was placed between the mirror plates of the interferometer, and the tubes in it were adjusted in position so that the fringe system was clearly visible. The furnace was gradually heated, and the temperatures were ascertained by means of a carefully calibrated glass thermometer. The temperature was controlled by a rheostat in the heating circuit, and no difficulty was experienced in maintaining the tubes at any desired temperature.

Table I.

Temperature.	Density of saturated Hg vapour.
° C.	grm./c.c.
100	0·0000021
110	0·0000040
260	0·0005830
270	0·0006528
280	0·0008645
300	0·0013466
305	0·0013882
310	0·0016447
320	0·0019879

The densities of the saturated mercury vapour for different temperatures were determined by interpolation from values recorded by F. B. Jewett,\* and are given in Table I.

The standard density selected was that of mercury vapour reduced to 0° C. and 76 cm. pressure, on the assumption that it obeyed the ordinary gas laws.

$$\begin{aligned} \text{i.e., } \rho_0 &= \frac{\text{density of hydrogen at N.T.P.} \times \text{At. wt. of mercury}}{\text{molecular wt. of hydrogen}} \\ &= \frac{0.0000899 \times 200.6}{2.002} \\ &= 0.009001 \text{ gm./c.c.} \end{aligned}$$

This, of course, is based on the assumption that mercury vapour is a monatomic gas. The lengths of the interferometer tubes were 26.0 cm., and were taken to be constant over the range of temperatures covered, since for a change of 300° C. the increase in length was not more than 1 part in 6000.

The results obtained with wave-length  $\lambda = 6230 \text{ \AA.U.}$ , which are typical of those obtained with other wave-lengths, are given in Table II.

Table II.

Wave-length $\lambda = 6230 \text{ \AA.U.}$					
Initial temperature.	Final temperature.	$\rho_1 - \rho_2$ .	$x$ .	$k = \frac{x}{\rho_1 - \rho_2}$ .	Mean value.
° C.	° C.				
110	322.5	0.002080	8.5	4090	Mean $k = 4078$ .  $\mu_0 - 1 = 0.000882$ .
110	320.0	0.001984	8.0	4080	
110	322.0	0.002060	8.4	4080	
110	322.0	0.002060	8.2	4000	
110	324.0	0.002139	9.0	4210	
110	322.5	0.002080	8.4	4040	
110	322.5	0.002080	8.5	4090	
110	322.0	0.002060	8.4	4080	
110	322.0	0.002060	8.4	4080	
110	322.0	0.002060	8.4	4080	

The refractive indices obtained with the four wave-lengths,  $\lambda = 4860 \text{ \AA.U.}$ ,  $\lambda = 5132 \text{ \AA.U.}$ ,  $\lambda = 6110 \text{ \AA.U.}$ , and  $\lambda = 6230 \text{ \AA.U.}$ , are given in the fourth column of Table III.

\* F. B. Jewett, 'Phil. Mag.', November, 1902, p. 546.

Table III.—Refractivity of Metallic Vapours.

Mercury of normal pressure and temperature.					
Jamin interferometer by Cuthbertson and Metcalfe.		Jamin interferometer by author.		Quartz prism by author.	
Wave-length $\lambda$ A.U.	Refractive index, $\mu_0$ .	Wave-length $\lambda$ A.U.	Refractive index, $\mu_0$ .	Wave-length $\lambda$ A.U.	Refractive index, $\mu_0$ .
5183	1·000943	4860	1·000949	4358·56 Hg	1·000942
5460·97 Hg	1·000941	5132	1·000943	5460·97 Hg	1·000902
5893 Na	1·000933	6110	1·000924	5780 Hg	1·000891
6563·04 H $\alpha$	1·000899	6230	1·000882	6234·31 Hg	1·000860

Thallium at temperature of 540° C. (German silver and copper thermo-couple).	
Quartz prism by author.	
Wave-length $\lambda$ A.U.	Index of refraction $\mu$ .
4358·56 Hg	1·000229
4861·49 H $\beta$	1·000110
5460·97 Hg	1·000293
5769·45 Hg	1·000222
5790·49 Hg	1·000144
5893 Na	1·000165
6234·31 Hg	1·000309
6563·04 H $\alpha$	1·000142

The results of Cuthbertson and Metcalfe, reduced to the same standard density, are given in the second column of the same table, and it will be seen the two sets of values present a fair agreement.

#### 5. Prism Experiments with Mercury Vapour.

In carrying out this set of experiments with mercury vapour, one of a number of prisms which had been made up was selected at random. Its refracting angle, which was large, was 93·5°. A quantity of mercury was put into the prism sufficient to fill the lower tube and part of the prism itself. The prism was then exhausted and hermetically sealed. It was then enclosed in an electric furnace of nichrome wire, temperatures being measured in this case with a thermo-couple of copper and German silver, which was carefully calibrated. The readings were taken with a millivoltmeter. The prism and furnace were mounted on a table of a finely constructed refractometer, with which readings could be taken to 1 second of arc.

As the deviations obtained were small, the ordinary formula for minimum deviation was modified as follows :—

$$\mu = \frac{\sin A + D/2}{\sin A/2} = \frac{\sin A/2 \cos D/2 + \cos A/2 \sin D/2}{\sin A/2},$$

$$= 1 + D/2 \cot A/2,$$

D being the angle of deviation of the ray and A the refracting angle of the prism.

If  $\mu$  is the refractive index of the vapour for the density  $\rho$ , and  $\mu_0$  the index for the standard density  $\rho_0$ , then we have

$$\frac{\mu_0 - 1}{\mu - 1} = \frac{\rho_0}{\rho} \text{ and } \mu - 1 = \frac{1}{2} D \cot \frac{A}{2},$$

or 
$$\mu_0 - 1 = \frac{\rho_0}{\rho} \frac{D}{2} \cot \frac{A}{2},$$

D, the angle of deviation being measured in radius.

As in the case of the interferometer experiments,  $\rho_0$  the standard density is given by

$$\rho_0 = \frac{\text{density of hydrogen at N.T.P.} \times \text{At. wt. of element}}{\text{molecular weight of hydrogen}}$$

$$= 0.009001 \text{ gm./c.c. for mercury.}$$

If the deviation of the ray in seconds be denoted by  $\delta$ , it follows that  $D = 4.852 \times 10^{-6} \delta$ , and substituting for D, in the formula given above,

$$\mu_0 - 1 = \rho_0 / \rho \times 2.426 \times 10^{-6} \cdot \delta \cdot \cot A/2$$

$$= \rho_0 / \rho \times 2.288 \times 10^{-6} \delta, \text{ taking } A \text{ to be } 93.5^\circ.$$

In making these prism measurements, the furnace and the enclosed prism were maintained at a temperature of  $320^\circ \text{C}$ . The density of the saturated mercury vapour at this temperature was taken from Jewett's values to be 0.001988 gm./c.c. Monochromatic light from a mercury arc lamp of wave-lengths  $\lambda = 4358.56 \text{ \AA.U.}$ ,  $\lambda = 5460.97 \text{ \AA.U.}$ ,  $\lambda = 5780 \text{ \AA.U.}$ , and  $\lambda = 6234.31 \text{ \AA.U.}$ , were used, the requisite radiations being obtained by the use of suitable Wratten and Wainwright filters.

As an indication of the magnitude of the measurements actually made, it may be stated that values were obtained for  $\delta$ , for the different wave-lengths used which ranged from 83 to 91 seconds of arc. The values of the refractive indices deduced are given in the sixth column of Table III; it will be seen they are slightly lower than those obtained in the interferometer determinations. They are, however, sufficiently in agreement with the latter to demonstrate the feasibility of using the prism method.



6. *Prism Experiments with Thallium Vapour.*

In the experiments with thallium vapour, the procedure followed was identical with that adopted in dealing with the mercury vapour, sufficient metallic thallium being used to fill, when melted, the lower tube and part of the prism itself. As the densities of saturated thallium vapour for different temperatures have not as yet been determined, the determination of the refractive indices was confined to readings taken with a density corresponding to a temperature of  $540^{\circ}$  C. The melting point of thallium is  $301^{\circ}$  C., and it was found that, at the temperature selected, the density of the vapour was sufficient to give readings on the refractometer, which could be made with ease and accuracy. In all, the refractive indices were determined for eight wave-lengths, the radiations used being obtained either from the mercury arc lamp or from a Geissler tube containing hydrogen.

The indices, as determined, are given in the eighth column of Table III, and are shown graphically in fig. 3.

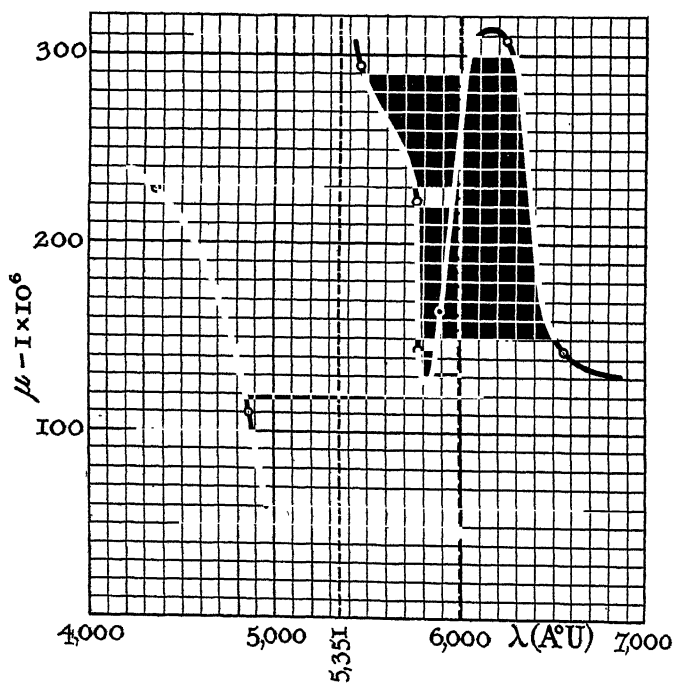


FIG. 3.

7. *Anomalous Dispersion with Thallium Vapour.*

From the form of the graph in fig. 3, it will be seen that anomalous dispersion is clearly indicated at the wave-length  $\lambda = 5350.65$  Å.U., and

probably also at or near the wave-length  $\lambda = 6000 \text{ \AA.U.}$  Direct experiments made by Guthrie\* failed in showing any absorption of this wave-length by non-luminous thallium vapour. It is known, however, from the work of Kayser and Runge,† that the wave-length  $\lambda = 5350.65 \text{ \AA.U.}$  is strongly reversed in the arc spectrum of thallium, and Hermann Geisler‡ has shown, too, that if light be passed through thallium, vapourised in the carbon arc, anomalous dispersion is obtained at this wave-length. The only direct observation of absorption by non-luminous thallium vapour at  $\lambda = 5350.65 \text{ \AA.U.}$  appears to be that obtained by G. E. Gibson§ under very exceptional conditions. In his experiments, he found that carefully purified thallium, when sealed within an evacuated clear fused quartz tube, and then heated in an electric oven to  $1300^{\circ} \text{ C.}$ , emitted the thallium green line strongly. This he showed to be a pure temperature effect. When, however, with the electric oven at  $1350^{\circ} \text{ C.}$ , the cold tube containing the thallium was inserted in the oven, he found, a short time after introducing the tube, that the reversed thallium line  $5460.65 \text{ \AA.U.}$  could be seen as a dark line on the continuous spectrum of the heated oven, which acted as a radiating black body.

From the experiments of Gibson, it would appear, therefore, that the anomalous dispersion indicated by the present investigation as existing at  $\lambda = 5350.65 \text{ \AA.U.}$  is very probably correct. It is not clear, however, why non-luminous thallium vapour, when tested directly by passing the light of a continuous spectrum through it, does not show absorption at  $\lambda = 5350.65 \text{ \AA.U.}$  It should also be stated that, up to the present, no investigator appears to have observed any absorption by non-luminous thallium vapour in the neighbourhood of  $\lambda = 6000 \text{ \AA.U.}$ , and that the nearest wave-length to  $\lambda = 6000 \text{ \AA.U.}$  in the emission spectrum of thallium appears to be that observed by Eder and Valenta|| with the spark at  $\lambda = 5949.08 \text{ \AA.U.}$

### 8. Results.

1. It has been shown that interferometer tubes and hollow prisms of clear fused quartz, free from distortion and all trace of devitrification, can be readily made by a new method.

2. With such tubes, determinations have been made of the refractive indices for a number of wave-lengths with the vapours of mercury and thallium.

\* Guthrie, 'Ast. Phys. Jl.,' vol. 29, No. 1, p. 211 (1909).

† Kayser and Runge, 'Wied. Ann.,' vol. 48, p. 126 (1893).

‡ Hermann Geisler, 'Inaug. Diss. University of Bonn,' January 20, 1909.

§ G. E. Gibson, 'Phys. Zeit.,' vol. 12, p. 1145, December 8, 1911.

|| Eder and Valenta, 'Wien. Ber.,' vol. 118, IIA, pp. 511, 1077 (1909).

3. The dispersion curve for non-luminous thallium vapour indicates the existence of anomalous dispersion at the wave-lengths  $\lambda = 5350.65 \text{ \AA.U.}$ , and probably also at or near the wave-length  $\lambda = 6000 \text{ \AA.U.}$

In conclusion, I desire to express my great appreciation of the help given me by my students, Messrs. H. Grayson Smith and L. W. Rentner, in taking the readings, and to that given me by my assistant, Mr. R. H. Chappel, in making up the interferometer tubes and prisms.

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*On the Emission and Absorption Spectra of Mercury.*

By Prof. J. C. McLENNAN, F.R.S., and W. W. SHAVER, M.A., University of Toronto.

(Received June 29, 1921.)

[PLATE 7.]

1. *Introduction.*

In two papers by Raymond C. Dearle\* accounts are given of investigations in which a special study was made of the monochromatic radiation  $\lambda = 1.014\mu$ . This radiation Paschen† found to be by far the strongest in the emission arc spectrum of mercury, and Dearle's observations corroborated this view.

Dearle found moreover, that when light of this wave-length was passed through non-luminous mercury vapour, even when of low density, a definite and well-marked absorption was obtained. He also found the same effect when the mercury vapour traversed was in direct contact with the mercury vapour in which the arc was established from which the original radiation was obtained, and was also directly illuminated by the radiation from this arc.

It is well known that the radiations whose frequencies are given by  $\nu = (1.5, S) - (2, p_2)$ , *i.e.*,  $\lambda = 2536.72 \text{ \AA.U.}$  and  $\nu = (1.5, S) - (2, P)$ , *i.e.*,  $\lambda = 1849.6 \text{ \AA.U.}$  are strongly absorbed by non-luminous mercury vapour, but no one as yet has been able to confirm the observations made by Dearle that the radiation  $\nu = (2, P) - (2.5, S)$ , *i.e.*,  $\lambda = 1.014\mu$  is absorbed by mercury vapour which is not luminous.

It is quite clear from the application of the quantum theory made by Bohr

\* Dearle, 'Roy. Soc. Proc.,' A, vol. 92, p. 608 (1916); vol. 95, p. 280 (1919).

† Paschen, 'Ann. der Phys.,' vol. 27 (13), p. 559 (1908).

to the problem of the origin of radiation that if mercury vapour were illuminated by radiation of frequency  $\nu = (1.5, S) - (2, P)$ , *i.e.*,  $\lambda = 1849.6 \text{ \AA.U.}$ , a certain number of the atoms of mercury in the vapour would have the configuration of their constituent extra-nuclear electrons so modified that they would be in the condition to absorb the wave-length  $\lambda = 1.014 \mu$ ; but in the absence of illumination by radiation of the wave-length  $\lambda = 1849.6 \text{ \AA.U.}$ , or of excitation of the mercury vapour by an equivalent stimulus, it is not clear how absorption of a radiation of the wave-length  $\lambda = 1.014 \mu$  by the mercury vapour could be obtained. If the effect observed by Dearle was correctly interpreted by him, it would mean that the atoms of ordinary mercury vapour would have in addition to the well-established resonance potential of 4.9 volts, corresponding to  $\lambda = 2536.72 \text{ \AA.U.}$ , an additional one of 1.26 volts, corresponding to  $\lambda = 1.014 \mu$ .

Although extensive investigations have been made on the resonance and ionisation potentials of many of the elements, there appears to be very little evidence obtainable from them which would go to support the suggestion put forward by Dearle that ordinary unexcited mercury atoms are really characterised by the two resonance potentials mentioned. Mercury atoms which have absorbed the radiation  $\lambda = 1849.6 \text{ \AA.U.}$  could, on the Bohr theory, possess the resonance potential 1.26 volts, but not mercury atoms whose electronic systems are in their ordinary stable configurations, provided views of the origin of radiations which are generally held at present remain valid.

As the suggestion put forward by Dearle as a result of his observations is of fundamental importance in connection with theories of atomic structure it was decided to set in train two lines of investigation with the object of clearing up the matter if possible. One of these investigations was undertaken by one of the authors of the present communication, and the second by the other. In the first investigation the photographic method was used, and in the other the method adopted involved the use of the spectrophotoelectric thalofide cell recently discovered by T. W. Case.\*

In both of the investigations no evidence was obtained of any measurable absorption of radiation of the wave-length  $\lambda = 1.014 \mu$  by non-luminous mercury vapour. In the case of luminous mercury, however, an easily measurable absorption of radiation of this wave-length was obtained when a thalofide cell was used to measure the intensities of the radiation.

\* T. W. Case, 'Phys. Rev.' [2], vol. 15, p. 289 (1920); also U.S. Patents Nos. 1301227 and 1316350 for a light reactive resistance.

## THE PHOTOGRAPHIC METHOD, by Prof. McLennan.

1. *Infra-red Photography.*

From the recently published accounts of the brilliant investigations carried out by Meggars,\* Kiess,† and Merrill,‡ it became abundantly clear that by the use of photographic plates stained with the dye dicyanin it was possible to photograph spectra as far as  $\lambda = 11650 \text{ \AA.U.}$ , and possibly beyond this limit.

As no photographs appeared to have been taken of the spectrum of mercury by these or other investigators with dicyanin-stained plates it appeared worth while attempting to take them. Considerable difficulty was experienced in obtaining dicyanin of good quality, but through the kindness of Dr. C. K. Mees of the Eastman Kodak Company some was finally obtained which enabled us to photograph spectra well up to the limit mentioned above.

2. *Photographic Results with Emission Spectra.*

Before proceeding to photograph the spectrum of mercury, it was considered best, in order to gain familiarity with the technique of the various operations, to make a study of the spectra of a number of the elements already investigated by Meggars and Kiess. In this work various types of plates were tried out, with both prism and grating spectrographs, the source of light being either a strong arc between metal electrodes or between carbon electrodes filled with salts of the various metals. In the case of mercury, ordinary commercial glass mercury-arc lamps, and also quartz mercury-arc lamps, were used.

With exposures up to six hours' duration, and a fairly fine spectrograph slit, the limit of Wratten and Wainwright panchromatic plates with moderate exposures was found to be about  $\lambda = 7000 \text{ \AA.U.}$ , and that of Ilford red sensitive plates about  $\lambda = 7500 \text{ \AA.U.}$  When ordinary rapid Seed dry plates, made by the Canadian Kodak Company, stained with dicyanin were used, spectra of moderate intensity were obtained, with a fine slit up to slightly over  $10000 \text{ \AA.U.}$ , with 12-17 hours' exposure. With a wide slit and 32 hours' exposure, spectra were obtained quite readily up to  $11137 \text{ \AA.U.}$ , with indications that in the case of very strong radiations this limit would be considerably extended.

The reproductions shown in (1), Plate 7, were obtained in photographing the

\* Meggars, 'Bulletin of the Bureau of Standards,' vol. 14, p. 371 (1917).

† Kiess and Meggars, 'Bulletin of the Bureau of Standards,' No. 324, p. 637 (1918); and No. 372, p. 51 (1920).

‡ Merrill, 'Bulletin of the Bureau of Standards,' No. 318, p. 487 (1918).

spectrum of the mercury arc in the near infra-red, and those in (2), when an attempt was made to extend the spectrum of mercury as far into the infra-red as possible. In obtaining (1) a quartz mercury-arc lamp was used, which was operated with a current of about three ampères under a potential difference of about 40 volts. The slit used was wide, about  $1\frac{1}{2}$  mm., and the exposure was about 32 hours. The spectrum was of the first order, the over-lapping portions of the higher orders being cut off by the use of a Wratten-Wainwright filter No. 22.

With the setting of the grating adopted in obtaining the spectrogram (*a*), (2), the wave-length  $\lambda = 10140$  Å.U. came, as the reproduction shows, somewhat near the end of the plate. A new setting of the grating was therefore made, which brought this wave-length somewhat more to the right of the plate. An exposure of 17 hours' duration was then made, with the lamp running under the same conditions as before, and with the same filter inserted. In this case, however, the slit was made about one-half as wide as it was in taking the first plate. The spectrogram obtained is that designated as "*b*," (2).

Reproduction "*a*," (2), shows that the radiation of wave-length  $\lambda = 10140$  Å.U. came out as a strongly marked diffuse wide band. The over-exposure was, however, too great to bring out the actual structure of the band. The plate from which reproduction "*b*" was taken was rather under-exposed, but in the original  $\lambda = 10140$  Å.U., though faint, could be seen quite definitely, either as a band about 60 Å.U. in width, with inversion at the centre over a range of about 20 Å.U., or a doublet with about 35 Å.U., or about 40 Å.U. separation between centres. In the reproduction the detail is not clear. The fact, as the reproduction shows, that wave-lengths slightly above and slightly below  $\lambda = 10140$  Å.U. came out clearly on the plate, rather points in the direction of inversion.

In reproduction "*c*," (3), which will be referred to later, the detail came out more definitely than in either "*a*" or "*b*." There it will be seen there is a strongly marked band at  $\lambda = 10217$  Å.U., a less strongly marked one at  $\lambda = 10165$  Å.U., and a fainter and narrower one at  $\lambda = 10121$  Å.U. The latter two would appear to make up what has hitherto been taken to be the wave-length  $\lambda = 10140$ , and the existence of the third strong band close to them at  $\lambda = 10217$  Å.U. would account for the strongly marked diffuse wide band shown in "*a*."

On measuring up the spectrograms of the mercury spectrum, it was found that wave-lengths were obtained up to  $\lambda = 11137$  Å.U., a number being recorded which had not been observed. These are given in the list collected in Table I, and are considered to be correct to 1 Å.U. The results obtained

by Wiedemann\* and by Stiles,† which appear to be the most complete hitherto recorded in the range covered by the present observations, are also given in the Table.

Table I.—Wave-Lengths from Mercury Arc.

Relative intensities.	Observer.		
	The Author.	Wiedemann.	Stiles.
	Å.U.	Å.U.	Å.U.
8	6908	6907·776	6907·74
	—	7044	—
10	7082·92	7082·273	7081·96
10	7092·46	7092·456	
	—	7122	
2	7179	7179	
1	7295	7295	
1	7371	7371	
2	7453	7453	
2	7551	7551	
2	7606	7606	
3	7673	7676	
8	7729·46	7729·456	
3	7821	7821	
2	7992	7982	
2	8028	—	
2	8077	8077	
1	8104	—	
1	8145	—	
3	8164	8164	
3	8198	8198	
1	8665		
1	8730		
1	8774		
1	8798		
1	8832		
1	9025		
1	9057		
3	9217		
3	9255		
3	9288		
1	9327		
1	9439		
1	9487		
1	9510		
1	9565		
1	9597		
1	9628		
1	9710		
1	9753		
2	9914		
2	9953		
2	9993		
2	10037		
2	10078		
30 {	10121 } 10140		
	10165 }		

\* Wiedemann, 'Ann. der Phys.,' vol. 38, p. 1041 (1912).

† Stiles, 'Astrophysical Journal,' vol. 30, p. 48 (1909).

Table I—(contd.)

Relative intensities.	Observer.		
	The Author.	Wiedemann.	Stiles.
	Å.U.	Å.U.	Å.U.
3	10217		
1	10301		
4	10344		
6	10377		
6	10416		
6	10453		
3	10485		
3	10531		
2	10567		
1	10845		
1	10874		
1	10883		
4	11053		
4	11088		
4	11101		
4	11137		

It will be seen that, in all, some forty-four new wave-lengths in the spectrum of mercury have been identified photographically. Of these,  $\lambda = 1.038 \mu$  and  $\lambda = 1.045 \mu$ , respectively, had been previously observed by McLennan and Dearle,\* and by Moll,† with a radiometric method involving the use of a linear thermocouple.

It may be that some of the wave-lengths given in the list are merely ghosts, for, in taking spectrograms with the same grating in the visible region, several of the strong lines in the spectrum of mercury were accompanied by them. Apart from this possible defect, however, the results are interesting, as showing that the wave-lengths of the radiation emitted by a luminous mercury vapour can be photographically recorded at least as far as  $\lambda = 11137 \text{ Å.U.}$ , and that we have in this way a new means of investigating the character of such important radiations as  $\lambda = 10140 \text{ Å.U.}$ , and of studying their specific properties.

### 3. Absorption Experiments.

In carrying out the absorption experiments, the procedure followed and the optical arrangements made, were, with one exception, identical with those adopted in obtaining the photograph of the emission spectrum of mercury, shown in reproduction "a," (2). The exception mentioned

\* McLennan and Dearle, 'Phil. Mag.,' vol. 30, November, 1915, p. 683.

† Moll, 'Kon. Akad. Wet. Amsterdam, Proceedings,' vol. 9, p. 544 (1907).



consisted in the insertion of a highly exhausted glass tube, 2.5 cm. in diameter, immediately in front of the slit.

A photograph was taken of thirty-two hours' duration, with this tube partly filled with mercury, and heated by an electric furnace to 300° C. In this case the tube was adjusted in position, so that the surface of the mercury was just below the bottom of the slit. At the temperature used it will be seen that the density of the mercury vapour traversed by the light was at least as high as that used in the experiments by Dearle.

A reproduction of part of the plate obtained in this case is shown in "c," (3). Accompanying it there is shown the corresponding portion of reproduction "a," (2). Through some stray light reaching it, either when in the spectrograph or in the developing room, the plate was slightly covered with a thin fog. It shows, however, quite definitely the wave-length  $\lambda = 10140$ . It is true this wave-length does not come out as a strongly marked broad band as in "a," but the difference was no doubt due to a part of the impinging light being reflected from or absorbed by the glass walls of the absorption tube.

It seems clear from the reproduction that there was little, if any, absorption by the mercury vapour in the absorption tube. If any absorption by the vapour did take place, it was extremely small compared with what one readily obtained with radiation of wave-lengths  $\lambda = 2536.72 \text{ \AA.U.}$  and  $\lambda = 1849.6 \text{ \AA.U.}$  It is true that the absorption of  $\lambda = 10140 \text{ \AA.U.}$  obtained by Dearle with non-luminous mercury vapour was only partial, but it was sufficiently well defined, according to his curves, to expect some indication of it on our photographic plates, if what he observed was a real absorption effect.

In so far, then, as these experiments go, they show that non-luminous mercury vapour does not absorb the radiation  $\lambda = 10140 \text{ \AA.U.}$  to the extent of appreciably weakening the photographic record of this wave-length.\* It would follow, then, that mercury atoms, with their electronic systems in their ordinary undisturbed state, do not have a resonance potential of 1.26 volts, and that therefore the true resonance potential for mercury atoms is the well established one, and corresponding to the quantum equivalent of  $\lambda = 2536.72 \text{ \AA.U.}$ , *i.e.*, to about 4.9 volts.

A number of wave-lengths were recorded on "c," (3), which were not strongly marked on either "a" or "b" of (2). Their values are given on the plate, and are also included in the list given in Table I.

\* From a note in 'Nature' of April 14, 1921, p. 203, the writer has just learned that the spectrum of mercury vapour has been recently photographed by A. Terenin up to  $\lambda = 11300 \text{ \AA.U.}$  In this investigation there was found no absorption by non-luminous mercury vapour of the radiation of wave-length  $\lambda = 10140$ .

The writer wishes to take this opportunity of expressing his appreciation of the help he received in making the optical arrangements, and in taking the photographs, from his research assistant, Mr. Vladimir Lubovich, of the University of St. Petersburg.

*Thalofide Cell Experiments.* By W. W. SHAVER.

1. *The Cell and its Properties.*

The thalofide cell used in these experiments was invented by and obtained from T. W. Case,\* of the Case Research Laboratory, Auburn, New York. The active part of this cell is a preparation of thallium-oxy-sulphide, fused on the surface of a quartz plate, the latter being securely mounted within an evacuated cylindrical glass flask, about 2.5 cm. in diameter. Evacuation was found to increase the sensitivity of the cell and to prevent deterioration through oxidation. The cell is photo-electrically sensitive in the near infra-red region from  $\lambda = 6000 \text{ \AA.U.}$  to  $\lambda = 12000 \text{ \AA.U.}$  The sensitivity curve, as given by Coblenz,† shows a sharp rise from  $\lambda = 6000 \text{ \AA.U.}$  up to  $\lambda = 9000 \text{ \AA.U.}$ , and then a further rise to  $\lambda = 10000 \text{ \AA.U.}$  From this wave-length on the sensitivity falls off rapidly, and is practically *nil* at  $12000 \text{ \AA.U.}$

The photo-electric sensitivity of this cell consists in a lowering of the electric resistance of the active preparation when it is exposed to radiations comprised within the limits mentioned. As the cell has its maximum sensitivity at or near  $\lambda = 10000 \text{ \AA.U.}$ , it was thought that it might prove specially suitable for studying radiation from mercury vapour of wave-length  $\lambda = 10140 \text{ \AA.U.}$ , and some preliminary experiments showed this conjecture to be well warranted.

The following is a short account of some experiments involving the use of this thalofide cell, and arranged with the object of investigating whether or not  $\lambda = 10140 \text{ \AA.U.}$  is absorbed by non-luminous and by luminous mercury vapour. It may be stated here that the results of the investigation go to show that  $\lambda 10140 \text{ \AA.U.}$  is not appreciably absorbed by non-luminous mercury vapour, but that it is absorbed to a marked extent by mercury vapour in which an arc of low intensity is maintained.

2. *Sensitivity Measurements.*

In commencing the investigation, some observations were made on the sensitivity of the cell when activated by light from a carbon-filament incandescent lamp, and by that from a quartz mercury arc lamp. Following

\* Case, 'Phys. Rev.', 1920, p. 289.

† Coblenz, 'Bureau of Standards,' Washington, No. 380, p. 253 (1920).

the instructions given by Paschen,\* Wratten filters Nos. H. 45 and F. 29, together with a water cell 1 cm. in thickness, were used to confine the light falling on the cell to the range of wave-lengths lying between  $\lambda = 8500 \text{ \AA.U.}$  and  $\lambda = 15000 \text{ \AA.U.}$  As the sensitivity of the cell is practically zero for  $\lambda = 12000 \text{ \AA.U.}$ , this arrangement resulted in the effective wave-lengths being necessarily limited to those between  $\lambda = 8500 \text{ \AA.U.}$  and  $\lambda = 12000 \text{ \AA.U.}$  Within this range the radiation of wave-length  $\lambda = 10140$  is, according to the observations of Dearle, by far the strongest in the light emitted by the mercury arc, and consequently in what follows it has been assumed that the effects obtained when the light from the mercury arc was used may be considered as being ascribable to the radiation  $\lambda = 10140 \text{ \AA.U.}$  In these experiments, with a carbon filament lamp of 32 candle-power, and a mercury-arc lamp, the former was placed at a distance of about 132 cm., and the latter at a distance of about 40 cm., from the active surface of the cell. The cell was joined in a series with a resistance of 240,000 ohms, a Tinsley galvanometer of 4000 ohms resistance and a storage battery having a potential difference of 4.72 volts. Readings were taken in millimetres on a scale at a distance of 1 metre from the galvanometer, and the sensitivity of the latter was such as to give 240 mm. deflection at 1 metre per microampère.

The unilluminated thalofide cell was found to give with this circuit a steady so-called "dark current" of 135 mm. deflection, but when the cell was illuminated this deflection was increased by an amount which depended on the intensity of the activating radiation as determined by the energy consumed by the source. Tables I and II contain the values of these added deflections, together with the corresponding amounts of energy supplied to the lamps.

Table I.—Carbon Filament Lamp

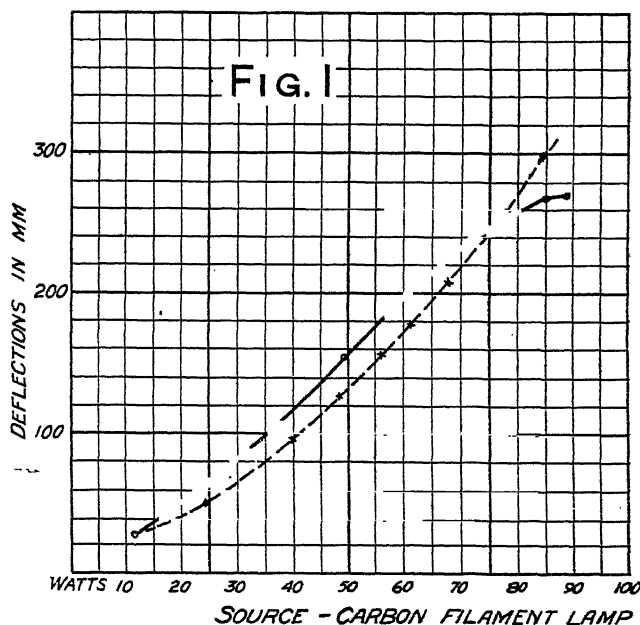
Source energy.	Increase in galvanometer deflection.	Source energy.	Increase in galvanometer deflection.
watts.	mm.	watts.	mm.
89.4	267	39.9	98
85.1	267	47.9	126
79.2	256	56.6	157
72.2	238	61.2	178
63.4	205	67.6	208
49.9	155	75.3	242
24.4	63	77.9	259
11.2	27	84.3	295
24.1	51		

\* Paschen, 'Wied. Ann.,' No. 43, p. 858 (1914).

Table II.—Mercury Arc Lamp.

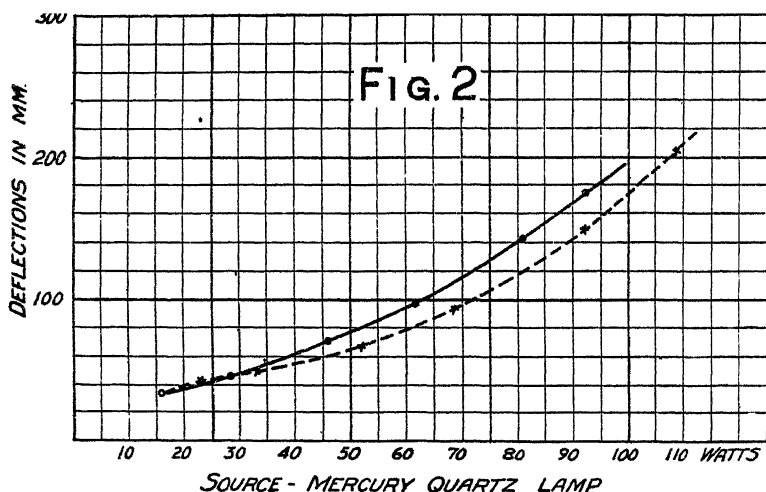
Source energy.	Increase in galvanometer deflection.	Source energy.	Increase in galvanometer deflection.
watts.	mm.	watts.	mm.
110.0	164	16.0	37
123.2	232	23.0	43
92.5	174	33.0	50
80.5	143	51.3	68
62.4	97	68.7	94
45.5	71	92.0	147
28.6	48	108.1	205

In figs. 1 and 2 graphs are drawn corresponding to the numbers in the Tables, the continuous curve representing the deflection obtained with a decreasing supply of energy and the broken one representing those obtained as the energy supplied to the lamp increased.



As the cell did not reach a steady state at once when being exposed to the radiation, all the readings were taken one minute after the commencement of each exposure. The lag shown by the curves was obtained when both lamps were used, and although it is known that it takes a considerable time for the quartz mercury arc lamps to settle down into a steady state after they are set in operation, it is thought that sufficient time was allowed after starting the

lamp for the steady state to be reached and that, therefore, the lag observed should be connected up, in the main, with the functioning of the thalofide



cell. From the values given in the Table it will be seen that under illumination an increase in current was easily obtained of twice the amount of the original "dark current."

### 3. Preliminary Absorption Experiments.

In these experiments the quartz mercury arc lamp was used as the source of radiation and the thalofide cell was provided with the filters mentioned in Section 2, the light being admitted to the cell through a slit about 2.5 mm. in width. When the lamp had reached a steady state and the galvanometer in series with the thalofide cell showed a steady deflection due to the illumination of 136 mm., an empty thin-walled pyrex glass bulb about 9 cm. in diameter was placed between the lamp and the filters. This produced a drop in the galvanometer deflection of 22 mm., due to reflection from or adsorption by its walls. A quantity of mercury was then placed in the bulb which was afterwards exhausted, hermetically sealed, and as previously, placed in the same position in the path of the light, care being taken to see that no mercury adhered to the walls of the bulb. In this case the fall in deflection due to the insertion of the bulb was practically the same as that obtained when it was empty. Heat was next applied to the bulb by means of an electric furnace and at the same time the walls of the bulb at the points of entrance and exit of the light were heated directly with auxiliary Bunsen burners, in order to prevent any deposit taking place from the mercury vapour. This was found to be necessary as it was observed that even a slight and scarcely

visible deposit of condensed vapour on the bulb walls immediately produced a marked decrease in the galvanometer readings.

In one particular set of readings with the mercury bulb at  $24^{\circ}$  C. an added deflection due to illumination of 151 mm. was obtained. When the bulb was heated to  $350^{\circ}$  C. the added deflection obtained was 152.5 mm. The consumption of energy by the lamp was checked during heating and it was found not to vary more than 1 per cent. From this it seemed clear that practically no absorption of the illuminating radiation took place. As mentioned above, the active radiation was confined to wave-lengths between  $\lambda = 8500 \text{ \AA.U.}$  and  $\lambda = 12000 \text{ \AA.U.}$ , and as  $\lambda = 10140 \text{ \AA.U.}$  was in all probability the most intense radiation in this range it seemed fair to conclude from these experiments that this wave-length was not appreciably absorbed by non-luminous mercury vapour.

#### 4. *Absorption Experiments with Non-luminous Mercury Vapour.*

(a) A series of experiments was then made with the activating radiation confined entirely to the wave-length  $\lambda = 10140 \text{ \AA.U.}$  With the grating used in the experiments described in the first part of this paper, it was possible to locate with precision from measurements on the photographic plates, the exact position of  $\lambda = 10140 \text{ \AA.U.}$  The thalofide cell was therefore mounted in a tube attached to a plate which fitted into the grooves of the plate holder so that it could be moved along the focal plane of the grating. The slit of the spectrograph was widened to about 1.5 mm., and a second slit of 4 mm. width was placed immediately in front of the thalofide cell to limit the radiation which could enter the latter from the grating. The light from a mercury arc lamp was projected on the slit of the spectrograph after passing through a Wratten filter No. 22, inserted to cut off the green, violet and ultra-violet radiation of the second order spectrum. The plate carrying the thalofide cell was then moved along the grooves in the focal plane to the point previously determined as the position of the focussed radiation of wave-length  $\lambda = 10140 \text{ \AA.U.}$  As soon as this position was reached, a large increase in the galvanometer deflection was at once obtained, and it was interesting to observe how accurately this wave-length could be located by the use of the thalofide cell. Movements of the latter in the focal plane in either direction were immediately followed by the disappearance of the galvanometer deflection in excess of that due to the "dark current."

When it was found that large readings could be readily obtained with the thalofide cell when the radiation was limited to the wave-length  $\lambda = 10140 \text{ \AA.U.}$ , an experiment was made to test the absorption of this particular wave-length by non-luminous mercury vapour.

The pyrex glass mercury vapour absorption tube used in the photographic experiments was mounted in the electric furnace and placed in front of the spectrograph slit in the path of the light from the mercury arc. This produced a drop in the galvanometer deflections of 30 mm., when the reading due to the direct radiation was 105 mm. The tube was then heated to 300° C., and the galvanometer readings were noted as the temperature of the vapour tube rose. No difference was observed in the galvanometer readings, the deflection being still 75 mm. when the temperature of 300° C. was reached. At this temperature it will be noted that the density of the mercury vapour was that corresponding approximately to atmospheric pressure. This experiment was repeated with a 300-watt argon-filled tungsten lamp as the source of radiation, and in this case also no absorption by the mercury vapour was observed.

(b) To make a more exacting test for absorption than that made in the previous experiment, two absorption tubes of pyrex glass, of exactly the same dimensions, 24.4 cm. in length and 2.5 cm. in diameter, were constructed with plane parallel plate windows cut from the same sheet of glass. Some mercury was put into one of the tubes, and then both were highly exhausted and hermetically sealed. The windows of the mercury tube were kept absolutely free from condensed vapour by being gently warmed by a heating circuit of nichrome wire wound about the two ends. The mercury absorption tube was mounted between the source of radiation and the spectrograph slit in such a way that it could readily be removed and the empty tube placed in an exactly similar position. Having obtained the "dark current" galvanometer deflection, the light from the source was allowed to fall on the spectrograph slit, after passing through the absorption tube. The increase in galvanometer deflection was noted as soon as it became steady, and then the empty tube was quickly substituted for the absorption tube. The deflection was again taken, and in this way any change of galvanometer deflection due to the absorption of the radiation of wave-length  $\lambda = 10140 \text{ \AA.U.}$  by the mercury vapour could be determined immediately.

The following Tables give the results of a series of pairs of readings, using both the mercury-arc and the argon-filled tungsten lamp as sources of the radiation  $\lambda = 10140 \text{ \AA.U.}$

From the Table it will be seen that when the mercury-arc lamp was used as the source of the radiation  $\lambda = 10140 \text{ \AA.U.}$ , the average of the readings obtained with the empty tube was the same as that of those obtained with the tube which had the mercury in it. When the tungsten lamp was used as the source of the radiation, practically the same result was obtained, as

the slight difference in the mean of the readings for the two tubes (0.4 per cent.) was well within the limits of experimental error.

Table III.—Mercury-Arc Lamp.

Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through		Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through	
(a) Mercury absorption tube.	(b) Empty tube.	(a) Mercury absorption tube.	(b) Empty tube.
mm.	mm.	mm.	mm.
64	65	66	68
64	64	61	59
66	65	59	56
63	63	—	—
62	63	70	69
58	58	70	75
—	—	69	69
66	65	67	69
70	70	69	66
70	70	59	61
70	69		
Mean .....	...	69.1	69.1

Table IV.—Tungsten Lamp.

Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through		Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through	
(a) Mercury absorption tube.	(b) Empty tube.	(a) Mercury absorption tube.	(b) Empty tube.
mm.	mm.	mm.	mm.
134	137	144	138
144	136	130	137
137	137	130	135
135	137	141	132
139	136	132	135
Mean .....	...	136.6	136.0

This experiment, therefore, makes it very clear that the radiation  $\lambda = 10140 \text{ Å.U.}$  is not absorbed to any appreciable extent by mercury vapour saturated at room temperature.

(c) A third experiment was made to test the absorption of  $\lambda = 10140 \text{ Å.U.}$  by saturated mercury vapour of various densities. The sources of the



radiation were again the quartz mercury-arc lamp and the tungsten argon-filled one. The absorption tube was the one referred to in "(b)," which contained some mercury. This tube was placed within an electric furnace, whose temperature was gradually raised to 350° C. Over this range of temperatures several sets of readings were taken with each of the lamps. A set of readings, taken with the mercury-arc lamp, as the source of the radiation  $\lambda = 10140 \text{ \AA.U.}$  is given in Table V, and a set taken with the tungsten lamp is given in Table VI.

Table V.—Mercury-Arc Lamp.

Temperature of tube.	Increase in galvanometer deflection over that due to "dark current."	Temperature of tube.	Increase in galvanometer deflection over that due to "dark current."
° C.	mm.	° C.	mm.
25	71	233	76
65	86	245	76
105	74	257	76
130	78	266	69
150	86	293	79
165	76	295	86
178	82	320	74
203	76	325	78
219	83	350	78

Table VI.—Tungsten Lamp.

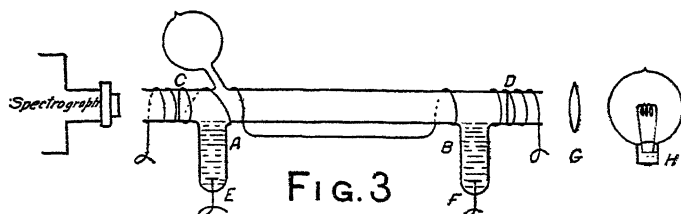
Temperature of tube.	Increase in galvanometer deflection over that due to "dark current."	Temperature of tube.	Increase in deflection over that due to "dark current."
° C.	mm.	° C.	mm.
22	135	187	141
28	140	203	139
40	138	211	138
58	135	225	136
78	138	240	134
103	136	260	134
117	136	290	132
138	136	320	138
155	138	350	135
171	141		

It will be seen that there was some irregularity in the readings given in the previous Tables, particularly when the mercury arc was used as a source of the radiation of wave-length  $\lambda = 10140 \text{ \AA.U.}$  This was due to unsteadiness in the voltage from the current supply mains, and in the case of the mercury-arc it was also caused by variations in the energy consumption of the lamp itself. However, from these readings it is clear that as the vapour density increased up to that corresponding to a pressure of one atmosphere,

there was, on the whole, no decrease in the galvanometer deflections. This showed that the amount of radiation of wave-length  $10140 \text{ \AA.U.}$  coming from the source through the absorption tube, was independent of the density of the mercury vapour in the tube, and therefore that the non-luminous mercury vapour did not absorb the radiation of this wave-length.

### 5. *Absorption Experiments with Luminous Mercury Vapour.*

In order to see whether luminous mercury vapour would absorb radiation of wave-length  $\lambda = 10140 \text{ \AA.U.}$ , a lamp A B, shown in fig. 3, was made up out



of pyrex glass. The ends of this lamp were closed by two sealed-in plane parallel plates of pyrex glass, as shown in the diagram. The lamp was partly filled with mercury as indicated, and it was then evacuated and sealed up. By means of two auxiliary heating coils the end-plates at C and D were kept hot and therefore free of any deposit from the mercury vapour. This lamp was placed before the slit of the spectrograph, as shown in the diagram, and the light from the source, H, containing radiation of the wave-length  $\lambda = 10140 \text{ \AA.U.}$  was focussed with the lens, G, on the slit after passing through the lamp A B. The thalofide cell as in the previous experiments was joined in series with a battery, a galvanometer and a high resistance, and was mounted in the focal plane of the grating so as to receive only the radiation of wave-length  $\lambda = 10140 \text{ \AA.U.}$  In these experiments, as in those previously described, the quartz mercury arc lamp and the tungsten lamp were used as sources of this radiation.

Readings were taken (1) of the "dark current" deflection when neither the source of light, H, nor the lamp, A B, were in operation; (2) when the pyrex lamp, A B was running with current just sufficient to maintain the arc; (3) when both the lamps, H and A B, were in operation; and (4) immediately after the arc in the pyrex lamp, A B, was extinguished, but while the source of light, H, was kept operating. From these readings it was possible to calculate the percentages of the radiation of wave-length  $\lambda = 10140 \text{ \AA.U.}$  from the source, H, absorbed by the vapour in the lamp, A B, when the latter was in the luminous state.

A summary of the results obtained from a number of these sets of readings is given in Table VII.

Table VII.

Source of radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$	Increase in deflection over the "dark current" galvanometer deflection due to			Percentage absorption.
	Light from pyrex lamp, mercury arc.	Light from pyrex lamp, mercury arc, and from source H after passing through luminous vapour in A B.	Light from source H after passing through non-luminous vapour in A B.	
Quartz mercury arc lamp	Column I. (mm.)	Column II. (mm.)	Column III. (mm.)	Column IV.
	28.5	109.0	98.0	17.9
	26.0	101.0	92.0	18.5
	26.5	100.5	90.5	18.2
	28.0	86.0	76.0	23.7
Tungsten lamp			Mean .....	19.6
	11.0	128.0	124.0	5.6
	15.5	141.5	136.5	7.7
	13.0	124.0	120.0	7.5
	20.5	188.5	178.5	6.4
			Mean .....	6.8

In calculating the percentage absorption given in column IV, the readings in column II were subtracted from the sum of the corresponding ones in columns I and III. These differences were divided by the corresponding numbers in column III, and were taken as measures of the fractional absorptions of the radiation by the luminous vapour. From these fractions the percentage absorptions easily followed.

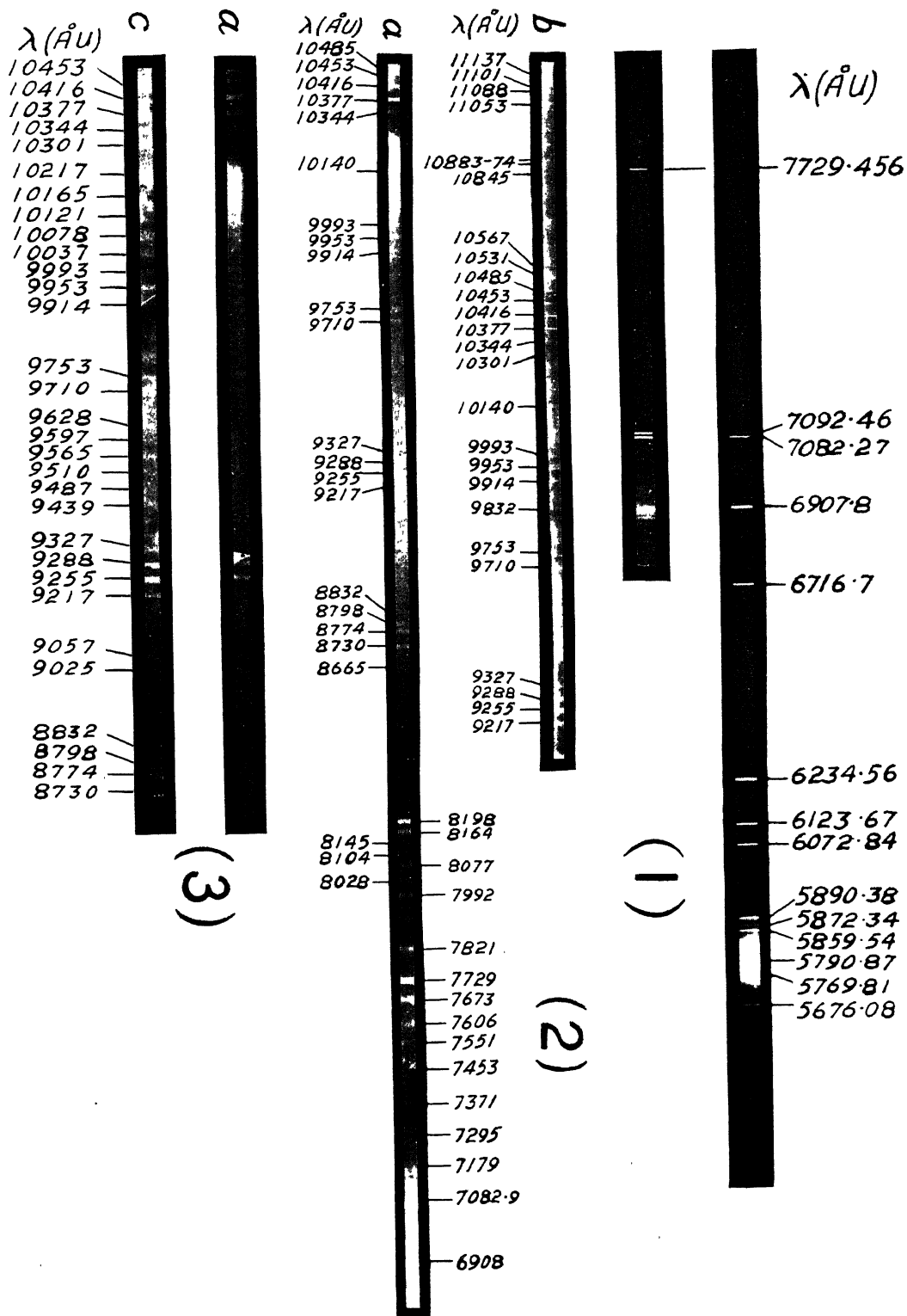
These experiments are interesting examples of the use of thalofide cells, and they will serve to indicate the advantages which are likely to accrue from the extensive use of these cells in the future as radiometers, when measurements of intensity are required to be made in the near infra-red region.

#### 6. *Summary of Results of both Investigations.*

(1) With plates stained with the dye dicyanin, the spectra of a number of the elements have been photographed in the infra-red region. In the case of mercury, the spectrum was photographed up to  $\lambda = 11137 \text{ \AA.U.}$

(2) By the photographic method, as well as by the use of thalofide cells, it has been shown that non-luminous mercury vapour does not absorb radiation of the wave-length  $\lambda = 10140 \text{ \AA.U.}$

(3) It has been found that slight and scarcely visible deposits of mercury vapour markedly absorb radiation of the wave-length  $\lambda = 10140 \text{ \AA.U.}$ , and this result may possibly afford an explanation of the observations made by Dearle.





(4) By the use of thalofide cells and low-intensity mercury arcs, it has been shown that radiation of the wave-length  $\lambda = 10140 \text{ \AA.U.}$  may be strongly absorbed by luminous mercury vapour.

(5) From the absence of absorption of radiation of wave-length  $\lambda = 10140 \text{ \AA.U.}$  by non-luminous mercury vapour, it follows that the atoms of mercury in their ordinary state do not possess a resonance potential of 1.26 volts, corresponding to  $\lambda = 10140 \text{ \AA.U.}$ , in addition to the well-established one of 4.9 volts, corresponding to  $\lambda = 2536.72 \text{ \AA.U.}$

*On the Structure of the Balmer Series Lines of Hydrogen.*

By J. C. McLENNAN, F.R.S., Professor of Physics, and P. LOWE,  
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(Received June 29, 1921.)

[PLATE 8.]

1. *Introduction.*

It is well known that the Balmer series of the hydrogen spectrum, under moderate resolution, consists of doublets. Numerous measurements have been made of the doublet separation for  $H_{\alpha}$ , but only a few of that for  $H_{\beta}$ . These are as follows:—

$H_{\alpha}$ .	$\Delta\lambda (\text{\AA.U.})$	$\Delta\nu (\text{cm.}^{-1}).$
Michelson and Morley* .....	0.11	0.253
Ebert† .....	0.132	0.306
Michelson‡ .....	0.14	0.323
Houstoun§ .....	0.065	0.153
Fabry and Buisson   .....	0.132	0.306
Meissner¶ .....	0.124	0.288
Merton and Nicholson** .....	0.132	0.306
Merton†† .....	0.145	0.34
Gehrcke and Lau‡‡ .....	0.126	0.293

\* Michelson and Morley, 'Phil. Mag.,' vol. 24, p. 46 (1887).

† Ebert, 'Wied. Ann.' (N.P.), vol. 43, p. 800 (1891).

‡ Michelson, 'Bur. Int. des Poids et Mesures,' vol. 11, p. 139 (1895).

§ Houstoun, 'Phil. Mag.,' vol. 7, p. 460 (1904).

|| Fabry and Buisson, 'C. R.,' vol. 154, p. 1501 (1912).

¶ See Paschen, 'Ann. der Phys.,' vol. 50, p. 933 (1916).

\*\* Merton and Nicholson, 'Roy. Soc. Proc.,' A, vol. 93, p. 28 (1917).

†† Merton, 'Roy. Soc. Proc.,' A, vol. 87, p. 307 (1920).

‡‡ Gehrcke and Lau, 'Phys. Zeit.,' vol. 21, p. 634 (1920).

$H_{\beta}$	$\Delta\lambda$ (Å.U.)	$\Delta\nu$ (cm. <sup>-1</sup> ).
Michelson .....	0.08	0.33
Merton and Nicholson .....	0.033	0.14
Merton .....	0.093	0.39
Gehrcke and Lau .....	0.0695	0.294

The only determinations which appear to have been made of the doublet separation for  $H_{\gamma}$  and  $H_{\delta}$  are those recently obtained by Gehrcke and Lau.\* Their result for  $H_{\gamma}$  is  $\Delta\lambda = 0.058$  Å.U. ( $\Delta\nu = 0.307$  cm.<sup>-1</sup>), and for  $H_{\delta}$  is  $\Delta\lambda = 0.0432$  Å.U. ( $\Delta\nu = 0.257$  cm.<sup>-1</sup>). The outstanding feature of the results given above, it will be seen, is the lack of agreement exhibited by the numbers for  $H_{\alpha}$  and  $H_{\beta}$ .

While some spectroscopists have taken the Balmer series to be a principal one, others have considered it to be a subordinate series. From an inspection of the values recorded above, it is difficult to reach a definite conclusion respecting the type to which the Balmer series should be assigned. The general trend of the numbers representing the frequency differences is in the direction of a decrease, with the progress of the series towards the violet. This might lead one to conclude the type was that of a principal doublet series. Such a conclusion, however, is scarcely warranted, for Gehrcke and Lau, who found for the doublet separation of the first four members,  $H_{\alpha} = 0.29$ ,  $H_{\beta} = 0.29$ ,  $H_{\gamma} = 0.3$ ,  $H_{\delta} = 0.26$  cm.<sup>-1</sup>—values which show a tendency gradually to decrease—have stated their results are to be taken as supporting the view that the frequency difference of the doublet components is constant for all members of the series. Departures from this law exhibited by their numbers are to be considered as coming within the limits of error of the observations.

In applying to hydrogen his theory of the fine structure of spectral lines, developed by extending Bohr's theory of the origin of radiations, and incorporating with it the principle of relativity, Sommerfeld† has shown that each member of the doublet  $H_{\alpha}$  should consist of a close triplet, each member of  $H_{\beta}$  of a close quartette, each member of  $H_{\gamma}$  of a close quintette, etc. He has shown, moreover, that his theory lends itself to the precise calculation of the intensities of these constituents of the doublets. Sommerfeld has found, too, that, theoretically, the magnitude of the doublet separation should be constant for all members of the Balmer series, and equal to

\* The investigation described in the present communication was begun, and measurements were made on the separation of the components of  $H_{\alpha}$ ,  $H_{\beta}$ ,  $H_{\gamma}$ , and  $H_{\delta}$ , before the publication of Gehrcke and Lau's paper.

† Sommerfeld, 'Ann. der Phys.,' vol. 51, p. 1 (1916); also 'Atombau und Spektrallinien,' p. 344.

$0.365 \text{ cm.}^{-1}$ . In the case of  $H_\alpha$ ,  $H_\beta$ , and  $H_\gamma$ , the calculated distribution and intensities of the fine structural components is such that, in actual determinations of the doublet separations, values less than  $0.365 \text{ cm.}^{-1}$  should be obtained. For  $H_\delta$ , and the higher members of the series, effects connected with the fine structure of the components of the doublets should be less in evidence. It follows, therefore, that in proceeding from  $H_\alpha$  to the higher members of the Balmer series, we should expect, on the basis of Sommerfeld's theory, to obtain for the doublet separations values that rapidly increase up to  $0.365 \text{ cm.}^{-1}$  for  $H_\delta$ , and then remain constant for the remainder of the series.

A direct test of Sommerfeld's theory, through an examination of the structure of the doublets of the Balmer series of hydrogen, is necessarily attended with considerable difficulty. With atoms so light as those of hydrogen, the Doppler effect arising from molecular thermal agitation is considerable at ordinary temperatures. As a result, the members of the doublets cannot ordinarily be obtained as sharp lines, but as broad and more or less diffuse bands. This diffuseness is, moreover, enhanced by the Stark effect, which always exists to a greater or less extent when the emission of radiation is brought about by electrical stimulation.

What has been taken to be a remarkable confirmation of the validity of Sommerfeld's theory has been obtained by Paschen,\* through a study of the structure of spectral lines belonging to series originating in the helium univalent ion. With this element the Doppler effect is less marked than with hydrogen, and, as the nuclear electric charge for helium atoms is twice as great as that for atoms of hydrogen, the lines of the spectrum of helium are less influenced than those of hydrogen by the Stark effect, and on that account are sharper.

In summing up the results of Paschen's observations, Sommerfeld has reached the conclusion that qualitatively and quantitatively, they constitute a definite and strong confirmation of his theory. A further confirmation is found in the fact that the L. series of the Röntgen spectra of the elements consists of doublets with a constant separation between the components of approximately  $0.365 \text{ cm.}^{-1}$ .

In discussing Sommerfeld's theory and its supposed confirmation by Paschen, Stark† has pointed out that a vital characteristic of the theory lies in its quantitative features. He has drawn attention in particular to Paschen's observations on the helium line  $\lambda = 4686 \text{ Å.U.}$  and has emphasised the latter's failure to find three components whose presence was demanded by the

\* Paschen, 'Ann. d. Phys.,' vol. 50, p. 933 (1916).

† Stark, 'Jahr. d. Radioakt. und Elek.,' vol. 7, Heft 2, No. 66, p. 170 (1920).



theory, and to his observation of a component whose presence was not predicted by it. Stark also makes a point of the fact that the observed relative intensities of the components of  $\lambda = 4686 \text{ \AA.U.}$  do not agree with the values calculated by Sommerfeld. Moreover, he lays particular stress on the fact that while Sommerfeld's theory indicates that the doublet separations in the Balmer series of the hydrogen spectrum should gradually increase in passing from  $H_\alpha$  to  $H_\delta$ , the results of Gehrcke and Lau, taken as they stand, show doublet separations gradually decreasing in magnitude as we pass from the first to the fourth member of the series.

From the above it will be seen that while strong confirmation of Sommerfeld's theory has been obtained from Paschen's investigation of the structure of a number of wave-lengths in the spectrum of helium, and from an important characteristic of the L. series in the Röntgen spectra of the elements, it is highly desirable to have the validity of the theory tested directly by making accurate determinations of the doublet separations of as many as possible of the members of the Balmer series of hydrogen.

The following paper aims at giving an account of an investigation initiated with this object in view. It will suffice to state here, that in our determinations of the doublet separations of  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$ , values were obtained which regularly decreased from  $0.36 \text{ cm.}^{-1}$  to  $0.29 \text{ cm.}^{-1}$  in passing from the first to the fourth member of the series.

## 2. Apparatus.

In this investigation the doublet separations were measured with a Lummer plate, for which the optical data were the following:—

### *Optical Data of Lummer Plate.*

	Refractive Indices.	
	$\lambda (\text{\AA.U.})$	$\mu$
$l = 13 \text{ cm.}$	6563.045	1.50746
$d = 0.448 \text{ cm.}$	5896.155	1.50990
$d\mu/d\lambda \text{ for } H_\alpha = - 324 \text{ cm.}^{-1}$	5890.186	
$H_\beta = - 716 \quad ,$	4861.49	1.51560
$H_\gamma = - 960 \quad ,$	4308.08	1.52025
$H_\delta = - 1150 \quad ,$		
$\Delta\lambda_m \text{ for } H_\alpha = 0.4159 \text{ \AA.U.}$		
$H_\beta = 0.2224 \quad ,$		
$H_\gamma = 0.1755 \quad ,$		
$H_\delta = 0.1550 \quad ,$		

The discharge tube made of pyrex glass, was similar in type to that used by Prof. R. W. Wood\* in photographing the higher members of the Balmer series. As fig. 1 shows, its central portion was surrounded by a glass

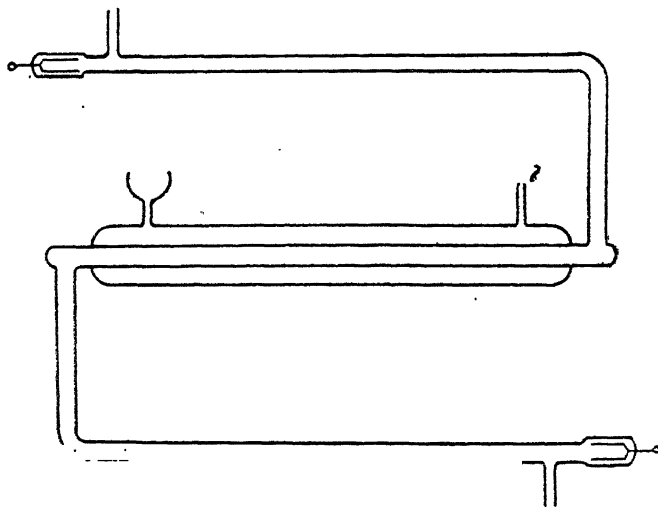


FIG. 1.

envelope that could be filled with liquid air when desired. This central portion was about 50 cm. in length, and 5 mm. in diameter. To obtain the spectrum a Hilger constant deviation spectrograph was used that was provided with a symmetrically opening slit at the entrance to the collimator tube, and with a second one at the exit of the observation tube. The light used was that which issued axially from the central position of the discharge tube. In taking photographs of the interference bands the Lummer plate was placed immediately behind the spectrograph in line with the axis of the observation tube, the fringes being brought to a focus in a camera provided with an achromatic lens of 30 cm. focus. The discharge tube was supplied with hydrogen generated in an ordinary voltameter by the electrolysis of dilute sulphuric acid. A  $\frac{1}{4}$ -kilowatt Clapp Eastham 15,000-volt transformer was used to produce the discharge and in most cases the transformer was operated with a current of about two ampères in the primary circuit.

### 3. *Experiments.*

In carrying out the experiments the hydrogen on issuing from the voltameter was led into the discharge tube after passing successfully through a drying tube filled with phosphorus pentoxide and a capillary tube curled into

\* R. W. Wood, 'Roy. Soc. Proc.,' A, vol. 97, p. 455 (1920).

a spiral about 4 cm. in diameter and 8 cm. in length. A Gaede rotary mercury pump was attached to the exit of the discharge tube and was kept continuously in operation while exposures were made. In assembling the apparatus a series of trials was made with capillary tubes of different bores and lengths, until one was found, which under the continuous operation of the Gaede pump allowed the hydrogen to flow into the discharge tube at a rate which kept the pressure in the latter constant, and at the value at which it was found the transformer would give the strongest illumination.

With the symmetrically opening slits mounted on the collimator and observation tubes of the constant deviation spectrograph, no difficulties were experienced in isolating the wave-lengths  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ,  $H_\delta$ . Repeated attempts were made with the same arrangement to isolate the higher members of the Balmer series, but they were not successful. The investigation was therefore limited to the determination of the doublet separations of the first four members of the series.

When the procedure outlined above was followed, it was found out that all four wave-lengths came out quite distinctly as doublets.

When, however, the discharge tube was kept surrounded with liquid air during the exposures, all four of the wave-lengths came out on the plate as triplets. At first it was thought that this pointed to a change produced in the structure of the lines of the Balmer series brought about by the use of liquid air. It was noted, however, on measuring up the plates that the separation of two members of each triplet was the same as the doublet separations found respectively for  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ,  $H_\delta$ , when operating at room temperatures. This suggested the possibility of hydrogen being contaminated with some impurity whose spectrum became enhanced in some way when the tube was surrounded with liquid air. The spectrum of the light from the discharge was then photographed, and it was found that as soon as the envelope surrounding the discharge tube was filled with liquid air, the spectrum of nitrogen came out on the plates with strong intensity. A tube filled with coconut charcoal was then inserted in the gas circuit between the capillary spiral and the discharge tube, and kept cold with liquid air. When this precaution was taken the wave-lengths  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$  again came out as comparatively sharp and clearly defined doublets.

Reproductions of these doublets are shown in Plate 8, (1). It will be seen that all four are clearly defined.

Reproductions of the triplets for  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$  are shown in (2). With  $H_\alpha$  and  $H_\gamma$  the third member of the triplets came out strongly, while with  $H_\beta$  it was comparatively weak. With  $H_\delta$  the third

member of the triplet was very strong, but the pair constituting the doublet only came out faintly. In the reproduction shown in (2) the components of the doublet for  $H_\beta$  are not discernible.

The different spectra obtained with the discharge tube are shown in (3). Reproduction "a" was obtained with the unpurified hydrogen when the discharge tube was at room temperature, and reproduction "b," when the discharge tube through which the unpurified hydrogen was passed, was cooled with liquid air. In this case it will be seen the spectrum of nitrogen was very strongly recorded. Reproduction "c" was obtained when hydrogen purified with liquid air-cooled cocoanut charcoal was passed through the tube, and the latter was kept at room temperature. Reproduction "d" is the spectrum of mercury. It will be seen from "b" that while  $H_\beta$  came out quite clear and at some distance from any of the wave-lengths of nitrogen which were visible,  $H_\alpha$ ,  $H_\gamma$ , and  $H_\delta$  were recorded in close proximity to wave-lengths in the nitrogen spectrum. The triplet structure was, however, obtained with  $H_\beta$ , as well as with  $H_\alpha$ ,  $H_\gamma$  and  $H_\delta$ , and this fact rather militates against the view that the third member of each of the triplets had its origin in nitrogen.

It will be seen that the secondary spectrum of hydrogen came out strongly in "c," and that it contained wave-lengths close to  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$ , but not close to  $H_\alpha$ . It may be, therefore, that the triplet structure actually arose from a modification produced by the nitrogen in the radiation emitted by the hydrogen.

#### *4. Doublet and Triplet Separations.*

In determining the separation of the components of the different wave-lengths, the plates were measured up with a Hilger photo-measuring micrometer, and readings were taken with it at the edges as well as at the centres of the interference bands. The mean values of the separation of the components of the four doublets,  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$ , taken from centre to centre, are given in Table I. The results of Merton and of Gehrcke and Lau are also given in the Table. It will be seen that the separation gradually decreased from 0.154 Å.U. for  $H_\alpha$  to 0.049 Å.U. for  $H_\delta$ , while the corresponding frequency differences dropped from 0.36  $\text{cm}^{-1}$  to 0.29  $\text{cm}^{-1}$ .

In fig. 2 the results are plotted with the wave-length differences as ordinates and the squares of the wave-lengths as abscissæ. Had the frequency difference for the components of the four wave-lengths been constant and equal to 0.365  $\text{cm}^{-1}$  the values of  $\Delta\lambda$  would have registered more or less closely with the continuous straight line through the origin. With the results obtained by us for the separations of the doublet components, however, the

Table I.

Line.	Wave-length $\lambda$ .	Separation of components.					
		Merton.		Gehrcke and Lau.		Authors.	
		$\delta\lambda$ .	$\delta\nu$ .	$\delta\lambda$ .	$\delta\nu$ .	$\delta\lambda$ .	$\delta\nu$ .
	$\text{\AA.U.}$	$\text{\AA.U.}$	$\text{cm.}^{-1}$	$\text{\AA.U.}$	$\text{cm.}^{-1}$	$\text{\AA.U.}$	$\text{cm.}^{-1}$
H $\alpha$	6563	0.145	0.34	0.126	0.29	0.154	0.36
H $\beta$	4861	0.093	0.39	0.070	0.29	0.085	0.36
H $\gamma$	4341			0.058	0.31	0.062	0.33
H $\delta$	4101			0.043	0.26	0.049	0.29

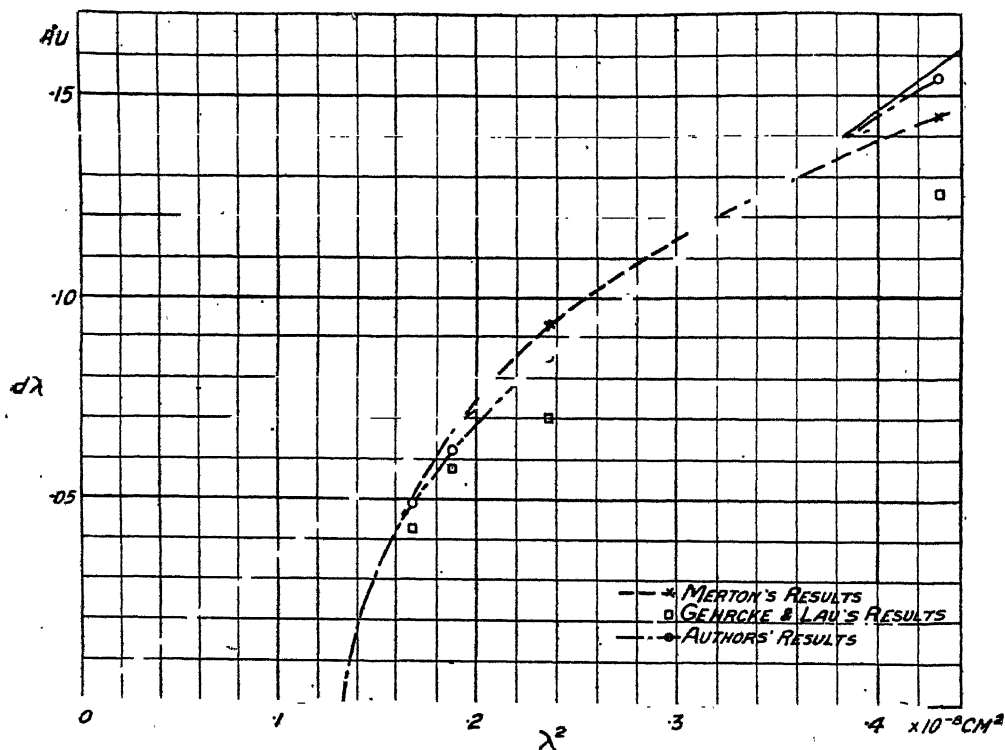
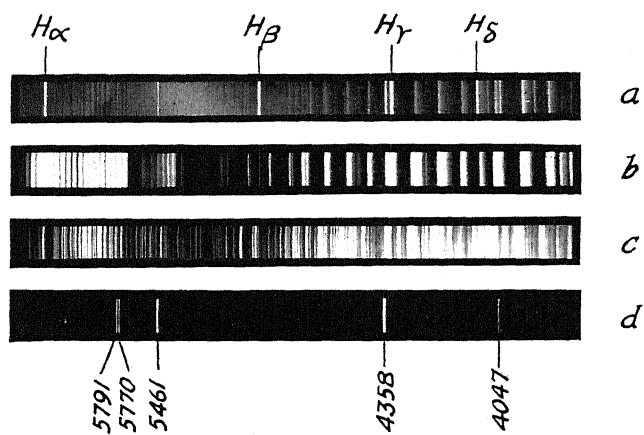
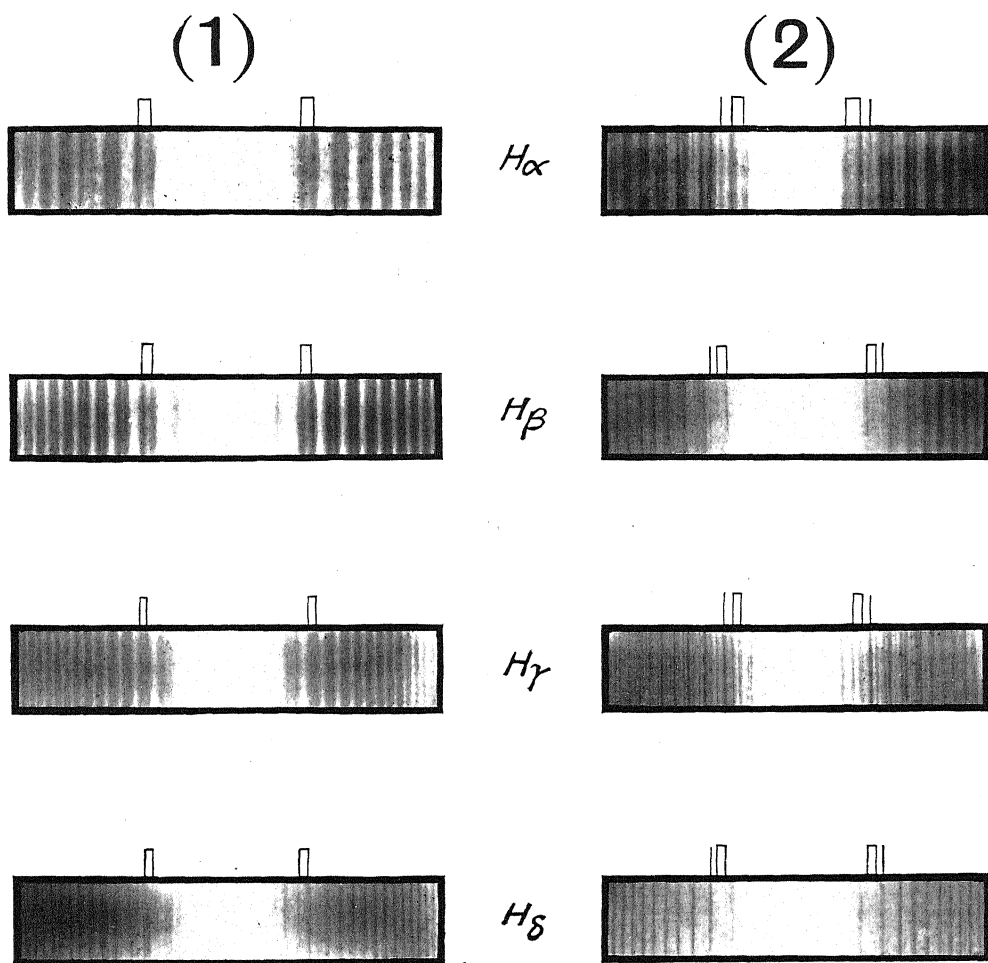


FIG. 2.

values of  $\Delta\lambda$  lay close to the broken curve which when extended, it will be seen, cuts the zero ordinate line at approximately  $0.133 \times 10^{-8} \text{ cm}^2$ . This would seem to indicate a separation of the doublets that vanishes at  $\lambda = 3648 \text{ \AA.U.}$  the limiting wave-length of the Balmer series. Should this result turn out to be correct it would show that the Balmer series of hydrogen should be classified as a principal rather than as a subordinate series.



(3)



In measuring up the plates on which the triplet structures were obtained difficulty was experienced in deciding whether the third member of the triplet had a wave-length longer than the long wave-length member of the corresponding doublet or shorter than the short wave-length member of the doublet. Attempts were made to settle the point by the use of a Lummer plate crossed with an échelon grating, but the results were not sufficiently satisfactory to settle the question. With the lengths of exposure it was found possible to use, the interference points were not clearly enough recorded on the plates:—

Table II.—Separation of Triplets.

Line.	Separation of		
	1 and 2.	2 and 3.	3 and 1.
	A.U.	A.U.	A.U.
H $\alpha$	0·154	0·123	0·140
H $\beta$	0·085	0·070	0·070
H $\gamma$	0·062	0·057	0·057
H $\delta$	0·049	0·048	0·057

The results of the measurements are recorded in Table II. In this Table "1" and "2" denotes the ordinary doublet separation, as observed by us, "1" being the longer wave-length member and "2" the shorter one. The designation "3" denotes the third member of the triplet. Under the heading "2" and "3," it is assumed that "3" is shorter in wave-length than "2," while under the heading "3" and "1" we have taken "3" to be longer than the wave-length "1."

If the third members of the triplets had their origin in the spectrum of nitrogen the measurements recorded in Table II would indicate that in the spectrum of this element there should be wave-lengths either at  $\lambda = 6563\cdot18$  Å.U. or  $6562\cdot89$  Å.U.,  $\lambda = 4861\cdot56$  Å.U. or  $4861\cdot41$  Å.U.,  $\lambda 4340\cdot72$  Å.U. or  $4340\cdot54$  Å.U.,  $\lambda = 4101\cdot91$  Å.U. or  $4101\cdot8$  Å.U.

In this connection it is interesting to note that, in the list of wave-lengths given for the spectrum of nitrogen by Kayser and Runge, wave-lengths are included at  $\lambda = 4861\cdot4$  Å.U.,  $\lambda = 4342\cdot0$  Å.U. and  $\lambda = 4101\cdot0$  Å.U.

As the secondary spectrum of hydrogen also includes wave-lengths at  $\lambda = 4860\cdot28$  Å.U., and  $\lambda = 4342\cdot07$  Å.U., the appearance of the triplet structure when the impure hydrogen was used, and its absence when the discharge was in the purified gas, is not altogether clear.



(5) *Summary of Results.*

(a) The following doublet separations were found for the first four members of the Balmer series  $H_\alpha = 0.154 \text{ \AA.U.}$ ,  $H_\beta = 0.085 \text{ \AA.U.}$ ,  $H_\gamma = 0.062 \text{ \AA.U.}$  and  $H_\delta = 0.049 \text{ \AA.U.}$

When these separations were plotted against the squares of the corresponding wave-lengths they were shown to lie on a curve which pointed to the vanishing of the doublet separation at the short wave-length limit of the Balmer series.

(b) The wave-lengths  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  and  $H_\delta$  have been shown to consist of triplets when the electric discharge takes place in hydrogen containing a trace of nitrogen.

(c) Experiments made to decide whether the third members of the triplets had their origin in the radiations emitted by nitrogen atoms or in a modification produced by the nitrogen in the radiations emitted by the atoms of hydrogen were not decisive.

*A Problem in the Theory of Heat Conduction.*

By J. W. NICHOLSON, F.R.S.

(Received September 29, 1921.)

The first problem discussed in this paper is as follows:—"A long hollow cylinder is immersed in a medium of uniform temperature, and at a certain instant, is brought suddenly to a temperature above that of the medium, for example, by the passage through it of a stream of heated liquid. It is *maintained* at that temperature, and the temperature distribution in the outside medium at any instant, and the rate of leakage of heat from the cylinder, are required."

The main difficulty arises from the fact that the law of temperature on the surface of separation is arbitrary—we shall suppose, in the first instance, that it is constant. Solutions for the external temperature distribution are apparently known only when the surface has a given *initial* distribution, which is left to adjust itself without further direct supply of heat.

A solution for the distribution inside a cylinder whose surface is kept at zero temperature, and whose interior has any initial distribution, has been known for some time, and may be obtained by several methods. Perhaps

the two most powerful methods of attack on problems of heat conduction are the synthetical method,\* which replaces the actual distribution by sets of sources and sinks distributed over the boundaries and throughout the region to be investigated, and the method which makes use of Green's functions. Naturally, it is in the theory of Potential that these functions are especially valuable, and their extension to problems of heat conduction, apparently noticed first by Minnigerode in his 'Göttingen Dissertation' of 1862, and since developed in some detail, notably by Betti and Carslaw, is still by no means completely worked out. Carslaw has, by a method dependent on contour integration, determined their forms in many interesting cases.

We may define the Green's function, after Carslaw, as "the temperature at a point  $(x, y, z)$  at time  $t$ , due to an instantaneous point source generated at  $(x_0, y_0, z_0)$  at time  $\tau$ , the bounding surface of the medium being maintained at zero temperature." With the help of the function so defined, we may show that

$$[v_P]_t = \iiint [u]_{\tau=0} f(x, y, z) dx dy dz + k \int_0^t d\tau \left[ \iint \phi(x, y, z, \tau) \frac{\partial u}{\partial n_2} dS \right],$$

where  $[v_P]_t$  is the temperature at a point, P, or  $(x_0, y_0, z_0)$  at time  $t$ , due to an initial temperature distribution  $f(x, y, z)$  at time  $t = 0$ , and the boundary, S, of the medium being kept at temperature  $\phi(x, y, z, t)$  at any subsequent time.

The thermometric conductivity of the medium is  $k$ , the equation of heat propagation being

$$\frac{\partial u}{\partial t} = k \nabla^2 u$$

and  $u$ , whose differentiation in the second integral is along the inward normal, is the function

$$u = \{4\pi k(t-\tau)\}^{-3/2} e^{-R^2/4k(t-\tau)},$$

where  $R$  is the distance between  $(x, y, z)$  and  $(x_0, y_0, z_0)$ . The formula is not quite identical with that of Carslaw in his main paper, where an error of sign appears to be present.

A direct proof that this expression satisfies the differential equation, with the initial and boundary conditions, is not difficult.

With similar notation, the corresponding solution for the two-dimensional problem, in which everything is independent of the co-ordinate  $z$ , becomes

$$[v_P]_t = \iint [u_{\tau=0} f(x, y) dx dy + k \int_0^t d\tau \left[ \int \frac{\partial u}{\partial n_2} \phi(x, y, \tau) dS \right],$$

the line integral being taken over the bounding arc, and the surface integral

\* Hobson, 'Proc. Lond. Math. Soc.,' vol. 19.

over any section of the medium perpendicular to  $z$ . The function  $u$  is now to be defined by

$$u = \{4\pi k(t-\tau)\}^{-1} e^{-R^2/4k(t-\tau)}$$

with  $R^2 = (x-x_0)^2 + (y-y_0)^2 = r^2 + r'^2 - 2rr' \cos(\theta - \theta')$

in terms of cylindrical co-ordinates whose axis is  $z$ , so that  $(r, r')$  denote normal distances from the axis, and  $(\theta, \theta')$  the orientations in the normal section, measured from some fixed initial line. The Green's function employed in this case is the temperature at a point  $(x, y)$  at time  $t$  due to a line source generated at the instant  $\tau$  along  $x = x_0, y = y_0$ , in the medium, the bounding surface being kept at zero temperature. In the application of the theorem, there are some difficulties which have not received attention, but these do not occur in this special case.

### *The Cylindrical Source.*

There is a simple expression for the temperature at any point at time  $t$  due to an instantaneous source of heat generated on the surface of a circular cylinder at  $t = 0$ , which has not received any specific notice. The corresponding formula for a point source in three dimensions, situated at the origin, is

$$u = Q(4\pi kt)^{-3/2} e^{-R^2/4kt}$$

at distance  $R = \sqrt{(x^2 + y^2 + z^2)}$ , where  $Q$  is the quantity of heat instantaneously generated and then left to itself. For a line source along the line  $x = x', y = y'$ , with a quantity  $Q$  per unit length,

$$u = Q(4\pi kt)^{-1} e^{-[(x-x')^2 + (y-y')^2]/4kt},$$

the source being created in each case at time  $t = 0$ . Consider now an infinitely long cylindrical source, with a quantity  $Q$  generated per unit length. The radius is  $a$ , and  $\theta$  is an orientation in any normal section. The quantity of heat generated in the strip of unit length between two generators subtending  $\delta\theta$  on the axis is

$$Q\delta\theta/2\pi$$

and this can be treated as a line source. By summation, the subsequent temperature due to the cylindrical source is

$$u = (4\pi kt)^{-1} \int_0^{2\pi} \frac{Q d\theta}{2\pi} e^{-(\rho^2 + a^2 - 2\rho a \cos \theta)/4kt}$$

at distance  $\rho$  from the axis. This becomes

$$u = \frac{Q}{4\pi kt} I_0\left(\frac{\rho a}{2kt}\right) e^{-(\rho^2 + a^2)/4kt},$$

where  $I_0$  is the Bessel function defined by

$$I_0(x) = J_0(ix).$$

*Cylindrical Surface Maintained at Temperature  $v_0$ .*

We now pass to the problem of more special interest, in which a temperature,  $v_0$ , which is constant, is established at  $t = 0$  over a cylindrical surface,  $\rho = a$ , and *maintained* at the value  $v_0$ .

The general theorem is not now applicable, for the space is not simply connected outside. The equation of conduction is modified at the surface, by the continual creation of heat. It is, moreover, different inside on account of the difference of  $k$ , the preceding theorem involving the same value of  $k$  throughout. Since the internal space is shut off by an arbitrarily prescribed surface temperature, the internal value of  $k$  cannot affect the external problem, and we might at first sight expect to find a theorem enabling us to write down the solution for the doubly-connected external space. But we shall find later that this is apparently impossible.

The general theorem will first be applied to the internal space, and the form of the result will suggest an appropriate type of external solution. This appears to be the first solution of its kind for the space outside a cylinder and by its nature we shall find it possible to determine the general solution corresponding to an arbitrarily maintained law of surface temperature.

The internal solution, composed of parts due to (1) the prescribed surface rigidity of distribution, and (2) the initial temperature, say  $v_0$ , from  $\rho = 0$  to  $\rho = a$ , may now be written down. It should be  $v = v_0$  permanently.

Denoting the parts of  $v$  corresponding to (1) and (2) by  $v_1, v_2$  respectively, we have

$$v_1 = -k \int_0^t d\tau \int \frac{\partial u}{\partial n_2} v_0 ds,$$

$$v_2 = \iint u_{\tau=0} v_0 dx dy.$$

The outward normal to the surface is along  $\alpha$  increasing, and therefore

$$\partial/\partial n_2 = -\partial/\partial \alpha,$$

and with

$$u = \{4\pi k(t-\tau)\}^{-1} e^{-R^2/4k(t-\tau)}$$

we have

$$v_1 = -kv_0 \int_0^t d\tau \{4\pi k(t-\tau)\}^{-1} \int_0^{2\pi} d\theta \cdot \alpha \frac{\partial}{\partial \alpha} \cdot e^{-R^2/4k(t-\tau)}.$$

But

$$R^2 = \rho^2 + a^2 - 2a\rho \cos \theta, \quad \partial R^2/\partial \alpha = 2(a - \rho \cos \theta),$$

and

$$v_1 = \frac{av_0}{8\pi k} \int_0^t \frac{d\tau}{(t-\tau)^2} \int_0^{2\pi} d\theta (a-\rho) \cos \theta e^{-R^2/4k(t-\tau)},$$

or with a new variable  $\beta$  defined by  $4k\beta(t-\tau) = 1$ ,

$$v_1 = \frac{av_0}{2\pi} \int_{\beta_0}^{\infty} d\beta \int_0^{2\pi} d\theta (a - \rho \cos \theta) e^{-\beta(\rho^2 + a^2 - 2a\rho \cos \theta)}$$

where

$$\beta_0 = 1/4kt.$$

This evidently becomes

$$v_1 = av_0 \int_{\beta_0}^{\infty} d\beta \{aI_0(2\rho a\beta) - \rho I_1(2\rho a\beta)\} e^{-\beta(\rho^2 + a^2)}.$$

This can be reduced by integration by parts, to

$$v_1 = \frac{1}{2} v_0 I_0 \left( \frac{\rho a}{2kt} \right) e^{-(\rho^2 + a^2)/4kt} - \frac{v_0}{2} (\rho^2 - a^2) \int_{\beta_0}^{\infty} d\beta I_0(2\rho a\beta) e^{-\beta(\rho^2 + a^2)},$$

the first term being its limiting value on the surface  $\rho = a$ .

Again the effect of the initial volume condition,—temperature  $v_0$  throughout the cylinder,—is

$$v_2 = v_0 \iint u_{\tau=0} dx dy,$$

the integration being over an internal section. Thus

$$\begin{aligned} v_2 &= \frac{v_0}{2kt} \int_0^a \sigma d\sigma \int_0^{2\pi} d\theta \cdot e^{-(\rho^2 + \sigma^2 - 2\rho\sigma \cos \theta)/4kt}, \\ &= \frac{v_0}{2kt} \int_0^a \sigma d\sigma I_0 \left( \frac{\rho\sigma}{2kt} \right) e^{-(\rho^2 + \sigma^2)/4kt}. \end{aligned}$$

The complete internal solution is  $v = v_1 + v_2$ , or

$$\begin{aligned} v &= \frac{v_0}{2kt} \int_0^a \sigma d\sigma I_0 \left( \frac{\rho\sigma}{2kt} \right) e^{-(\rho^2 + \sigma^2)/4kt} \\ &\quad + av_0 \int_{(4kt)^{-1}}^{\infty} d\beta \{aI_0(2\rho a\beta) - \rho I_1(2\rho a\beta)\} e^{-\beta(\rho^2 + a^2)}. \end{aligned}$$

The two integrals concerned in this formula are of very different types, and have not hitherto been related in the literature concerned with the Bessel functions. Nevertheless, there is clearly a remarkable relation between them, for the solution must be  $v = v_0$ .

We shall apply the Bessel-Fourier double integral to establish this connection, and to suggest the external solution. In the meantime, we notice that this theory of heat conduction gives a proof of a historical theorem of Weber. For the effect of a distribution of temperature  $v = v_0$  at all points of space initially must be a temperature  $v_0$  for all time. Accordingly, extending the integral in  $v_2$  to infinity, we must have

$$2kt = \int_0^{\infty} \sigma d\sigma I_0 \left( \frac{\rho\sigma}{2kt} \right) e^{-(\rho^2 + \sigma^2)/4kt},$$

or if

$$p^2 = 1/4kt, \quad m = \rho/2kt,$$

$$\int_0^\infty \sigma d\sigma I_0(m\sigma) e^{-\rho^2\sigma^2} = \frac{1}{2p^2} e^{m^2/4p^2},$$

which is Weber's formula.

*Application of the Bessel-Fourier Integral.*

Let us consider the formula

$$u = \int_0^\infty z J_0(\rho z) dz e^{-z^2 kt} \int_0^\infty r J_0(rz) f(r) dr$$

which satisfies the equation of heat conduction

$$\partial u / \partial t = k \nabla^2 u$$

by direct substitution, and which, when  $t = 0$ , gives  $u = f(\rho)$  by the Bessel-Fourier theorem. Clearly  $u$  is the temperature at any point of space at time  $t$ , due to the initial distribution,  $f(\rho)$  depending only on  $\rho$ , established at  $t = 0$  and left to itself.

Let us choose the initial distribution as a uniform temperature,  $v_0$ , from  $\rho = 0$  to  $\rho = a$ , and a uniform zero temperature from  $\rho = a$  to  $\rho = \infty$ . Then the subsequent temperature at any point is

$$u = \int_0^\infty z dz J_0(\rho z) e^{-z^2 kt} \int_0^a r J_0(rz) v_0 dr.$$

Since  $f(r) = v_0$  from  $r = 0$  to  $a$ , and zero beyond. But

$$\int_0^a r J_0(rz) dr = \frac{a}{z} J_1(az),$$

and therefore

$$u = av_0 \int_0^\infty dz J_0(\rho z) J_1(az) e^{-z^2 kt}.$$

Since this must be identical with the previous  $v_2$ , we have the remarkable formula

$$\int_0^\infty \sigma d\sigma I_0\left(\frac{\rho\sigma}{2kt}\right) e^{-(\rho^2+\sigma^2)/4kt} = 2akt \int_0^\infty dz J_0(\rho z) J_1(az) e^{-z^2 kt}.$$

This can also be proved analytically as follows:—

If  $f(\rho)$  is the integral on the left-hand side, it is equal, by the Bessel-Fourier theorem, to

$$f(\rho) = \int_0^\infty z J_0(\rho z) dz \int_0^\infty r J_0(rz) dr \int_0^\infty \sigma d\sigma I_0\left(\frac{r\sigma}{2kt}\right) e^{-r^2/4kt}$$

on interchanging the last two integrations, as their nature allows,

$$f(\rho) = \int_0^\infty z J_0(\rho z) dz \int_0^a \sigma d\sigma e^{-\sigma^2/4kt} \int_0^\infty r J_0(rz) I_0\left(\frac{r\sigma}{2kt}\right) e^{-r^2/4kt}.$$

The last integral is one of Weber's, having the value

$$2kt J_0(\sigma z) e^{-z^2 kt + \sigma^2/4kt}$$

and thus

$$\begin{aligned} f(\rho) &= 2kt \int_0^\infty z dz J_0(\rho z) e^{-z^2 kt} \int_0^a \sigma d\sigma J_0(z\sigma) \\ &= 2akt \int_0^\infty dz J_0(\rho z) J_1(az) e^{-z^2 kt} \end{aligned}$$

which demonstrates the identity.

Accordingly, in a preceding section,

$$v_2 = av_0 \int_0^\infty dz J_0(\rho z) J_1(az) e^{-z^2 kt}.$$

We next examine  $v_1$ : since by Weber's formula

$$I_0\left(\frac{\rho a}{2kt}\right) e^{-(\rho^2 + a^2)/4kt} = 2kt \int_0^\infty z dz J_0(\rho z) J_0(az) e^{-z^2 kt},$$

we may note, in passing, an elegant form for the effect of a cylindrical source. For an instantaneous generation of heat on a cylindrical surface  $\rho = a$  at  $t = 0$ , of amount  $Q$  per unit length, the subsequent temperature at all internal or external points is

$$v = \frac{Q}{2\pi} \int_0^\infty z dz J_0(\rho z) J_0(az) e^{-z^2 kt}.$$

Again

$$I_1\left(\frac{\rho a}{2kt}\right) e^{-(\rho^2 + a^2)/4kt} = 2kt \int_0^\infty z dz J_1(\rho z) J_1(az) e^{-z^2 kt},$$

and therefore

$$(aI_0 - \rho I_1) e^{-(\rho^2 + a^2)/4kt} = 2kt \int_0^\infty z dz \{aJ_0(\rho z) J_0(az) - \rho J_1(\rho z) J_1(az)\} e^{-z^2 kt}.$$

But

$$\frac{\partial}{\partial z} \cdot z J_1(az) = az J_0(az),$$

and therefore integrating by parts, the integrated terms vanishing

$$\begin{aligned} \int_0^\infty dz J_0(\rho z) J_0(az) e^{-z^2 kt} &= 2kt \int_0^\infty z^2 dz J_0(\rho z) J_1(az) e^{-z^2 kt} \\ &\quad + \rho \int_0^\infty dz J_1(\rho z) J_1(az) e^{-z^2 kt}, \end{aligned}$$

so that, for all positive values of  $t$ ,

$$\begin{aligned} (aI_0 - \rho I_1) e^{-(\rho^2 + a^2)/4kt} &= 4k^2 t^2 \int_0^\infty z^2 dz J_0(\rho z) J_1(az) e^{-z^2 kt} \\ &= \frac{1}{4\beta^2} \int_0^\infty z^2 dz J_0(\rho z) J_1(az) e^{-z^2/4\beta} \end{aligned}$$

with  $4kt\beta = 1$ .

Thus  $v_1$ , in preceding section, becomes

$$\begin{aligned} v_1 &= av_0 \int_0^\infty z^2 dz J_0(\rho z) J_1(az) \int_{\beta_0}^\infty \frac{d\beta}{4\beta^2} e^{-z^2/4\beta} \quad \left(\beta_0 = \frac{1}{2kt}\right) \\ &= av_0 \int_0^\infty dz J_0(\rho z) J_1(az) \{1 - e^{-z^2 kt}\}, \end{aligned}$$

and finally,  $v_1 + v_2$  is given by the simple form

$$v_1 + v_2 = av_0 \int_0^\infty dz J_0(\rho z) J_1(az)$$

whose value is  $v_0$  when  $\rho$  is less than  $a$ . We do not dwell upon some of the interesting formulæ of pure mathematics which can be derived from the above analysis.

### *The External Space.*

Integrals of the types

$$\int_0^\infty dz f(z) \{J_0(\rho z), \quad Y_0(\rho z)\} e^{-z^2 kt}$$

are now clearly most suitable for this space,  $Y_0$  being the second function defined by

$$Y_0(x) = \left\{ \frac{\partial J_n(x)}{\partial n} - (-)^n \frac{\partial J_{-n}(x)}{\partial n} \right\}_{n=0}$$

after Hankel, the function  $J_0$  alone being clearly insufficient. Consider then the formula

$$v = v_0 - v_0 \int_0^\infty dz f(z) \{J_0(\rho z) Y_0(az) - Y_0(\rho z) J_0(az)\} e^{-z^2 kt}.$$

This satisfies the differential equation,  $f(z)$  not involving  $\rho$  or  $t$ . Certain restrictions on  $f(z)$  may, of course, be necessary to secure convergency. The expression takes the value  $v_0$  when  $\rho = a$ , for all time, so that the condition of *maintained* constant surface temperature is satisfied. It also takes the value  $v_0$  at all points after an infinite time, as is necessary. It is therefore the solution we seek if it vanishes everywhere outside the surface  $\rho = a$  at time  $t = 0$ , or, analytically, if

$$\int_0^\infty f(z) dz \{J_0(\rho z) Y_0(az) - Y_0(\rho z) J_0(az)\} = 1$$

for all values of  $\rho$  greater than  $a$ . This serves to determine  $f(z)$ .

The generalisation of the Bessel-Fourier theorem given by Orr\* is peculiarly suitable for a problem of this type. Apparently it has never been applied as yet to any physical problem, although a procedure which is somewhat parallel, with series instead of integrals, can be traced in some of

\* 'Proc. R. Irish A.,' Sect. A, vol. 27, 1907-9.



Carslaw's papers. As enunciated by Orr, the theorem states that for values of  $\rho$  between  $a$  and  $b$ , the value of the integral

$$\int_0^\infty \lambda d\lambda \int_a^b r \phi(r) dr u_n(r, a) u_n(\rho, a) / K_n(i\lambda a) K_n(-i\lambda a)$$

where  $u_n(r, a) \equiv K_n(i\lambda r) K_n(-i\lambda a) - K_n(-i\lambda r) K_n(i\lambda a)$  is  $-\pi^2 \phi(\rho)$  at ordinary points, and

$$-\frac{1}{2} \pi^2 \{ \phi(\rho - \epsilon) + \phi(\rho + \epsilon) \}_{\epsilon=0}$$

at a point  $\rho$  where  $\phi$  may have a possible discontinuity, the mean on the two sides of the discontinuity being then required. There are no discontinuities in the space external to the cylinder with which we deal, so that the value will be  $-\pi^2 \phi(\rho)$  at the point  $\rho$ . The same integral is equal to zero when  $\rho = a$ , and to  $-\frac{1}{2} \pi^2 \phi(\rho - \epsilon)$  when  $\rho = b$ .

The function  $K_n$  in the above statement is the function which, in wave theory, is appropriate to a disturbance diverging from the origin, and is defined by

$$\frac{2 \sin n\pi}{\pi} K_n(x) = i^n J_{-n}(ix) - i^{-n} J_n(ix).$$

When  $n$  becomes an integer, it is easy to evaluate  $K_n$  in terms of  $J$  and  $Y$  functions. We find that Orr's theorem takes the form, where  $\phi$  is an arbitrary function,

$$\begin{aligned} \int_0^\infty \lambda d\lambda \int_a^b \frac{\{J_n(\lambda \rho) Y_n(\lambda a) - Y_n(\lambda \rho) J_n(\lambda a)\} \{J_n(\lambda r) Y_n(\lambda a) - Y_n(\lambda r) J_n(\lambda a)\}}{Y_n^2(\lambda a) + \pi^2 J_n^2(\lambda a)} r \phi(r) dr, \\ = \frac{1}{2} \{ \phi(\rho - \epsilon) + \phi(\rho + \epsilon) \} \quad \text{if } b > \rho > a \\ = 0 \quad \text{if } \rho = a \\ = \frac{1}{2} \phi(\rho - \epsilon) \quad \text{if } \rho = b. \end{aligned}$$

In our problem,  $b$  will ultimately be infinite. We require  $\phi(\rho) = 1$  between  $\rho = a$  and  $\rho = b$ .

Putting  $n = 0$ , and identifying the above double integral with the statement

$$\int_0^\infty dz f(z) \{J_0(\rho z) Y_0(az) - Y_0(\rho z) J_0(az)\} = 1$$

we at once obtain

$$v = v_0 - v_0 \int_0^\infty \frac{\lambda d\lambda \{J_0(\lambda \rho) Y_0(\lambda a) - Y_0(\lambda \rho) J_0(\lambda a)\}}{Y_0^2(\lambda a) + \pi^2 J_0^2(\lambda a)} F(\lambda) e^{-\lambda^2 k t}$$

where  $F(\lambda) = \int_a^b r dr \{J_0(\lambda r) Y_0(\lambda a) - Y_0(\lambda r) J_0(\lambda a)\}.$

This is the general solution for the region, initially at zero, between two cylinders of radii  $(a, b)$ , maintained since  $t = 0$  at temperatures  $(v_0, \frac{1}{2} v_0)$  respectively.

Removing the outer cylinder to infinity, or writing  $b = \infty$ , we obtain the solution of the original problem proposed. Thus, the process being justified by the convergent integral finally obtained, we write

$$F(\lambda) = \left( \int_0^\infty - \int_0^a \right) r dr \{ J_0(\lambda r) Y_0(\lambda a) - Y_0(\lambda r) J_0(\lambda a) \}.$$

But

$$\int_0^a \lambda r J_0(\lambda r) dr = \left[ r J_1(\lambda r) \right]_0^a = a J_1(\lambda a),$$

$$\int_0^a \lambda r Y_0(\lambda r) dr = \left[ r Y_1(\lambda r) \right]_0^a = a Y_1(\lambda a) + \frac{2}{\lambda}$$

where the expression

$$Y_0(x) = 2J_0(x) \left\{ \log \frac{x}{2} + \gamma \right\} - \frac{2}{x} - \frac{x}{2} - \dots$$

with  $x$  small, has been used. Moreover, the integrals from zero to infinity are well known to converge to the values

$$\int_0^\infty \lambda r J_0(\lambda r) dr = 0, \quad \int_0^\infty \lambda r Y_0(\lambda r) dr = \frac{2}{\lambda}$$

when  $\lambda$  is not itself zero.

Thus

$$\lambda F(\lambda) = a J_0(\lambda a) Y_1(\lambda a) - a Y_0(\lambda a) J_1(\lambda a) = -\frac{2}{\lambda}$$

using a well known property of the functions.

More generally, with an upper limit,  $b$ , for the integrals,

$$\lambda F(\lambda) = -\frac{2}{\lambda} - b \{ J_0(\lambda a) Y_1(\lambda b) - Y_0(\lambda a) J_1(\lambda b) \}.$$

Now, if the first value  $(-2/\lambda)$  of  $F(\lambda)$  is substituted in the integral for  $u$ , this integral is still convergent. The reason for this is that the exponential factor secures convergence at the upper limit, however small it may be, provided that it is not actually zero. The denominator  $Y_0^2 + \pi^2 J_0^2$  can never be zero, and the numerator never large, since the Bessel functions are oscillatory. Moreover, near the lower limit, on expanding the Bessel functions, the integrand behaves like

$$-\frac{\log a - \log \rho}{\lambda (\log \lambda)^2}$$

and the integral of  $\lambda^{-1}(\log \lambda)^{-2}$  is proportional to  $(\log \lambda)^{-1}$ , which *vanishes* with  $\lambda$ . Accordingly, the final integral is finite, and we are justified in removing the cylindrical boundary of radius  $b$  to infinity—this justification was not immediately obvious.

For the temperature outside the cylinder of radius  $a$ , maintained at  $v_0$  from  $t = 0$  onwards, we finally deduce the expression

$$v = v_0 + 2v_0 \int_0^\infty \frac{d\lambda}{\lambda} \cdot \frac{J_0(\lambda\rho) Y_0(\lambda a) - Y_0(\lambda\rho) J_0(\lambda a)}{Y_0^2(\lambda a) + \pi^2 J_0^2(\lambda a)} e^{-\lambda^2 k t}.$$

When  $t = 0$ , convergence is secured by the Bessel functions themselves at all points except  $\rho = a$ , where the integral becomes zero through a discontinuity. The generality of this mode of solution of problems of *maintained* temperature will be evident later. At the same time, the form of this solution is perhaps a sufficient indication that it will not in general be possible to find an analytical theorem for the external space, of a similar character to that quoted in connection with the Green's function for the internal space.

*The Leakage of Heat from the Cylinder.*

Let  $c$  be the specific heat and  $D$  the density of the external medium. Then the quantity of heat leaking by conduction from a length,  $l$ , of the cylinder in unit time is given by

$$h = -2\pi a c D \left( \frac{\partial v}{\partial \rho} \right)_{\rho=a}.$$

We may find this differential coefficient from the previous expression for  $v$  if the result is a convergent integral. Conditions of continuity, which are necessary, are satisfied at all external points by the nature of the integral. Thus,

$$\left( \frac{\partial v}{\partial \rho} \right)_{\rho=a} = -2v_0 \int_0^\infty \frac{d\lambda \{ J_1(\lambda a) Y_0(\lambda a) - Y_1(\lambda a) J_0(\lambda a) \}}{Y_0^2(\lambda a) + \pi^2 J_0^2(\lambda a)} e^{-\lambda^2 k t},$$

or since  $J_1(\lambda a) Y_0(\lambda a) - Y_1(\lambda a) J_0(\lambda a) = -2/\lambda a$

we find that the rate of loss of heat from length  $l$  is

$$h = 8\pi k c D v_0 l \int_0^\infty \frac{d\lambda}{\lambda} \cdot \frac{e^{-\lambda^2 k t}}{Y_0^2(\lambda a) + \pi^2 J_0^2(\lambda a)}.$$

When  $t = 0$ , this is instantaneously infinite, as we should expect, on physical grounds, for  $Y_0^2 + \pi^2 J_0^2$  behaves near the upper limit like  $2\pi/\lambda a$ —by the known asymptotic expansions of the functions concerned—but, for all subsequent time,  $h$  is finite, tending, as it should, to zero after an infinite time.

The total heat lost from a length,  $l$ , at a time,  $t$ , after the start is

$$\begin{aligned} H &= \int_0^t h dt \\ &= 8\pi c D v_0 l \int_0^\infty \frac{d\lambda}{\lambda^3} (1 - e^{-\lambda^2 k t}) / \{ Y_0^2(\lambda a) + \pi^2 J_0^2(\lambda a) \} \\ &= 8\pi c D v_0 l a^2 \int_0^\infty \frac{d\omega}{\omega^3} (1 - e^{-\omega^2 \beta}) / \{ Y_0^2(\omega) + \pi^2 J_0^2(\omega) \} \end{aligned}$$

where  $\beta = kt/a^2$ .

In this form, the integral is a function only of  $\beta$ , and can be tabulated by quadratures, and the use of the standard tables, now existing, of  $J_0(\omega)$ ,  $Y_0(\omega)$ . For practical purposes, it would be more convenient to possess an approximate formula for the heat lost between two epochs  $t_1, t_2$ , not very close to the starting point. This quantity of heat is given by

$$H' = 8\pi c D v_0 l a^2 \int_0^\infty \frac{d\omega}{\omega^3} (e^{-\omega^2 \beta_1} - e^{-\omega^2 \beta_2}) / \{Y_0^2(\omega) + \pi^2 J_0^2(\omega)\}.$$

Now if  $t$  be not too small, the magnitudes

$$(\beta_1, \beta_2) \equiv k/a^2 (t_1, t_2)$$

will ordinarily be large, so that the exponentials secure that the important parts of the integral shall come from the range near  $\omega = 0$ . We may then write

$$J_0(\omega) = 1, \quad Y_0(\omega) = 2(\log \omega/2 + \gamma)$$

where  $\gamma$  is Euler's constant. Thus approximately

$$H' = 8\pi c D v_0 l a^2 \int_0^\infty \frac{d\omega}{\omega^3} (e^{-\omega^2 \beta_1} - e^{-\omega^2 \beta_2}) \left/ \left\{ \pi^2 + 4 \left( \log \frac{\omega}{2} + \gamma \right)^2 \right\} \right.$$

which can be calculated rapidly by quadratures. We do not pursue this problem beyond the point of obtaining an exact solution.

*Cylindrical Surface maintained at any arbitrary Law of Temperature.*

*Conduction into the External Space.*

The mode of procedure towards a solution of this more general problem is now fairly clear. Suppose that an indefinitely long cylindrical surface is maintained from  $t = 0$ ,—when everything was at zero temperature—at a temperature  $F(t)$ . It is required to find the temperature at an external point.

Let it be possible to find an integral expression of  $F(t)$  in the form— $\alpha$  and  $\beta$  being constants—

$$F(t) = \int_a^\beta f(\lambda) e^{-\lambda^2 k t}$$

where  $k$  is the thermometric conductivity of the external medium. The majority of ordinary functions admit this possibility. Then the function

$$v_1 = \int_a^\beta f(\lambda) \frac{J_0(\lambda \rho)}{J_0(\lambda a)} e^{-\lambda^2 k t} d\lambda$$

is a solution of the equation of heat conduction, which takes the value  $F(t)$  when  $\rho = a$ . It will constantly preserve the appropriate arbitrary temperature on the surface, but it presupposes an initial distribution of temperature

$$(v_1)_{t=0} = \int_a^\beta f(\lambda) \frac{J_0(\lambda \rho)}{J_0(\lambda a)} d\lambda$$

at all external points  $\rho > a$ . This difficulty may be removed by the addition of another solution of the equation of heat conduction, of the form

$$v_2 = \int_0^\infty g(\lambda) \{J_0(\lambda\rho) Y_0(\lambda a) - Y_0(\lambda\rho) J_0(\lambda a)\} e^{-\lambda^2 kt} d\lambda$$

where  $g(\lambda)$  is to be determined. This expression necessarily vanishes when  $\rho = a$ , and  $g(\lambda)$  must be so chosen that at all other points, initially, the preceding distribution is cancelled. We thus choose  $g(z)$  to satisfy the equation

$$\int_0^\infty dz g(z) \{J_0(z\rho) Y_0(za) - Y_0(z\rho) J_0(za)\} = - \int_a^\rho f(x) \frac{J_0(\rho x)}{J_0(ax)} dx$$

for all values of  $\rho$  greater than  $a$ .

But by Orr's formula, when  $\rho$  lies between  $a$  and infinity,

$$J_0(x\rho) = \int_0^\infty z dz \cdot \frac{J_0(z\rho) Y_0(za) - Y_0(z\rho) J_0(za)}{Y_0^2(za) + \pi^2 J_0^2(za)} \\ + \int_a^\infty r dr J_0(rx) \{J_0(rz) Y_0(az) - Y_0(rz) J_0(az)\}.$$

Now, by a familiar procedure, we can prove directly from the differential equations for the functions that

$$\int_a^\infty r J_0(xr) J_0(zr) dr = \frac{a}{z^2 - a^2} \{x J_1(ax) J_0(az) - z J_1(az) J_0(ax)\}, \\ \int_a^\infty r J_0(xr) Y_0(zr) dr = \frac{a}{z^2 - a^2} \{x J_1(ax) Y_0(az) - z Y_1(az) J_0(ax)\},$$

and accordingly, on reduction,

$$\int_a^\infty r dr J_0(rx) \{J_0(rz) Y_0(az) - Y_0(rz) J_0(az)\} \\ = \frac{az}{z^2 - a^2} J_0(ax) \{Y_1(az) J_0(az) - J_1(az) Y_0(az)\} \\ = \frac{2J_0(ax)}{x^2 - z^2},$$

which is a comparatively simple expression. Substituting this in the double integrals we find, when  $\rho > a$ ,

$$\frac{J_0(x\rho)}{J_0(ax)} = -2 \int_0^\infty \frac{z dz}{x^2 - z^2} \cdot \frac{J_0(z\rho) Y_0(za) - Y_0(z\rho) J_0(za)}{Y_0^2(za) + \pi^2 J_0^2(za)}.$$

a very remarkable formula of a quite new type. The "principal value" of the integral with regard to the point  $x = z$  is understood to be taken.

It is fairly clear that more detailed analysis is not in fact necessary or suitable at this point, for it would encumber the main argument, and we are

only attempting to sketch the general method which is effective for such problems. We deduce at once that  $g(z)$  must be defined by

$$\begin{aligned} \int_0^\infty dz g(z) \{J_0(z\rho) Y_0(za) - Y_0(z\rho) J_0(za)\} \\ = - \int_a^\beta f(x) \frac{J_0(x\rho)}{J_0(xa)} dx \\ = 2 \int_0^\infty \frac{z dz \{J_0(z\rho) Y_0(za) - Y_0(z\rho) J_0(za)\}}{Y_0^2(za) + \pi^2 J_0^2(za)} \int_a^\beta \frac{f(x) dx}{x^2 - z^2} \end{aligned}$$

whence we may select

$$g(z) = \frac{2z}{Y_0^2(za) + \pi^2 J_0^2(za)} \int_a^\beta \frac{f(x) dx}{x^2 - z^2}$$

and then

$$v_2 = \int_0^\infty g(\lambda) d\lambda \{J_0(\lambda\rho) Y_0(\lambda a) - Y_0(\lambda\rho) J_0(\lambda a)\} e^{-\lambda^2 kt}.$$

The whole solution of the problem of heat conduction may then be expressed in the following terms:—

If the whole of space is at zero temperature, and a distribution of temperature  $v_0 = F(t)$  is established at  $t = 0$  suddenly, and afterwards maintained, over a cylindrical surface  $\rho = a$ , then the temperature at all external points at time  $t$  is given by

$$\begin{aligned} v = \int_a^\beta d\lambda f(\lambda) \frac{J_0(\lambda\rho)}{J_0(\lambda a)} e^{-\lambda^2 kt} \\ + \int_0^\infty \frac{2\lambda d\lambda \{J_0(\lambda\rho) Y_0(\lambda a) - Y_0(\lambda\rho) J_0(\lambda a)\}}{Y_0^2(\lambda a) + \pi^2 J_0^2(\lambda a)} e^{-\lambda^2 kt} \int_a^\beta \frac{f(x) dx}{x^2 - \lambda^2} \end{aligned}$$

where  $f(x)$  and the limits  $\alpha, \beta$  are defined by

$$F(t) = \int_a^\beta f(x) e^{-x^2 kt}$$

—or perhaps a group of integrals of this exponential type.

As a single illustration, let

$$F(t) = \frac{t}{c^2 + t^2}$$

where  $c$  is constant. Then since

$$\begin{aligned} \frac{t}{c^2 + t^2} &= \int_0^\infty e^{-\mu^2 t} \cos \mu c d\mu \\ &= 2k \int_0^\infty x dx \cos kcx^2 e^{-x^2 kt} \quad (\mu = cx^2), \end{aligned}$$

we have in this case,

$$\alpha = 0, \quad \beta = \infty, \quad f(x) = 2kx \cos kcx^2$$

and the solution which maintains the temperature

$$F(t) = \frac{t}{c^2 + t^2}$$

for all time over  $\rho = a$ , is

$$v = 2k \int_0^\infty \lambda d\lambda \cos k c \lambda^2 \frac{J_0(\lambda \rho)}{J_0(\lambda a)} e^{-\lambda^2 k t} \\ + 4k \int_0^\infty \frac{\lambda d\lambda \{J_0(\lambda \rho) Y_0(\lambda a) - Y_0(\lambda a) J_0(\lambda \rho)\}}{Y_0^2(\lambda a) + \pi^2 J^2(\lambda a)} e^{-\lambda^2 k t} \int_0^\infty \frac{x \cos k c x^2}{x^2 - \lambda^2} dx$$

and these integrals can be much reduced.

Further illustrations, and further reduction of such a solution into other forms readily possible, do not seem necessary. Our object has been served by the indication of the general solution of problems involving a prescribed temperature variation over a cylinder.

This general solution can be made to apply to the internal space by using Orr's theorem between the limits zero and  $a$ . Any initial distribution which is not zero may be treated for both spaces by superposition.

*A Study of Catalytic Actions at Solid Surfaces. Part VII.—The Influence of Pressure on the Rate of Hydrogenation of Liquids in Presence of Nickel.*

By E. F. ARMSTRONG, D.Sc., F.R.S., and T. P. HILDITCH, D.Sc.

(Received October 3, 1921.)

In Parts I, II and V\* of this series we have indicated the reasons which lead us to believe that during the catalytic hydrogenation of liquids the function of the metallic catalyst is to combine with both agents—the unsaturated organic compound and hydrogen—and produce an unstable intermediate complex. The experimental evidence has furthermore impressed upon us the conviction that the determining factor in hydrogenation is the degree of affinity displayed between nickel and the unsaturated compound; whilst we have had ample opportunity to observe the selective nature of the process as exemplified by the widely-varying rates of absorption of hydrogen characteristic of various definite types of organic compounds, we have not

\* Part I, 'Roy. Soc. Proc.,' A, vol. 96, pp. 137–146 (1919); Part II, *ibid.*, A, vol. 96, pp. 322–329 (1919); Part V, *ibid.*, A, vol. 98, pp. 27–40 (1920).

been fortunate enough to obtain experimental proof of the mode in which nickel effects the actual introduction of hydrogen to an organic molecule.

We have, therefore, directed our attention to the influence of the concentration of hydrogen on the rate of hydrogenation of liquids, and have examined a wide range of unsaturated organic compounds with respect to the rates at which they absorb hydrogen under varying pressures. Existing data on this subject are scanty, but indicate, in the case of the hydrogenation of fatty oils, that the rate of action is simply proportional to the pressure.\* On the other hand, it has been suggested† that the action of nickel is to adsorb the hydrogen (at the same time dissociating it into the atomic condition‡) and that it is the atomic hydrogen which interacts with the ethylenic linkage; if this were the case the acceleration induced by increasing the gas-pressure should be proportional to the square root of the latter.

The experiments now recorded were made in essentially the same apparatus as that described in Part I§ of this series; a small gas-compressor was however, inserted between the inlet gas meter and the hydrogenation vessel, the pressure being reduced again to atmospheric at the exit from the latter. In this way it was possible to obtain accurate continuous readings of hydrogen absorption, the actual gas-volumes being measured at atmospheric pressure.

The pressure in the system was allowed to reach the desired limit some moments before readings were commenced, the meters were then checked against each other, and readings taken at short intervals. Hydrogen absorption time curves were plotted in the ordinary way and the absorptions per minute under varying pressures over corresponding ranges of the absorption curves were then compared.

The results of the investigation were very definite and fall into three divisions:—

(i) *Normal*.—In the absence of substituent groups of the kind discussed below (iii) and in presence of sufficient nickel (in general so long as at least 0·1 per cent. of nickel is present), the ethylenic union is hydrogenated at a rate which is in almost exact proportion to the absolute pressure of the hydrogen.

(ii) *Subnormal*.—At very low concentrations of catalyst (*e.g.*, 0·01 to 0·02 per cent. of nickel reckoned on the organic compound) the increase in

\* Moore, Richter, and van Arsdell, 'J. Ind. Eng. Chem.,' vol. 9, p. 541 (1917); Maxted, 'J. Soc. Chem. Ind.,' vol. 40, pp. 169–171 T (1921).

† Thomas, 'J. Soc. Chem. Ind.,' vol. 39, pp. 120–124 T (1920); Lewis, 'J. Chem. Soc.,' vol. 117, pp. 623–638 (1920).

‡ Sieverts, 'Zeitsch. Physik. Chem.,' vol. 77, pp. 591–613 (1911).

§ *Loc. cit.*, p. 138.



rate of hydrogenation becomes less than proportional to the increase in pressure. The compounds which absorb hydrogen most readily are in general more prone to show this subnormal effect when the catalyst concentration is diminished, and it is especially marked in the case of multi-ethylenic compounds such as derivatives of linoleic acid or linolenic acid, or citral.

(iii) *Abnormal*.—If the unsaturated compound contains another group which has affinity towards nickel (but is not open to hydrogenation), we find that increase in hydrogen pressure causes an increase in the rate of hydrogen absorption in more than simple proportion to the altered concentration of hydrogen.

This has been observed with unsaturated alcohols and unsaturated carboxylic acids: the carboxyl group tends, of course, to act upon nickel producing the nickel salt of the acid and hydrogen, although at the higher temperatures of hydrogenation ( $180^{\circ}$  C.) the equilibrium is moving in the direction of reduction of the salt by hydrogen to free acid and metallic nickel. The hydroxyl group in alcohols is also affected by nickel, although the latter is not, strictly speaking, an active catalyst of dehydration; thus, numerous instances have been recorded of side actions in the hydrogenation of the vapours of unsaturated alcohol over nickel in which formation of a hydrocarbon and water occur (*e.g.*, phenol at  $180^{\circ}$  C. yields cyclohexanol mixed with a little cyclohexanone and cyclohexene;\* benzylalcohol gives toluene and methylcyclohexane;† geraniol yields some dimethyloctane as well as the saturated dimethyloctanol‡). On the other hand, unsaturated aldehydes and ketones have shown, in each case which we have examined, increases in rate of absorption of hydrogen in simple, or less than simple, proportion to the pressure, so that we may summarise the results as follows:—

Unsaturated compound.	Effect of pressure.
Alcohols $R\cdot CH:CH\cdot CH_2(OH)$ .....	Abnormal.
Aldehydes (ketones) $R\cdot CH:CH\cdot CHO$	Normal (or subnormal).
Acids $R\cdot CH:CH\cdot COOH$ .....	Abnormal.

This behaviour is in keeping with the generalisation outlined above, since the carbonyl residue CO is, in contrast to the hydroxyl and carboxyl groups, open to direct hydrogenation.

The results are broadly, then, that increase in concentration of hydrogen causes a directly proportionate increase in the rate of hydrogenation,

\* Sabatier and Senderens, 'Compt. Rend.,' vol. 137, p. 1025 (1903).

† Sabatier and Senderens, 'Bull. Soc. Chim.' [3], vol. 33, p. 616 (1905).

‡ Enklaar, 'Ber.,' vol. 41, p. 2085 (1908).

providing there are no disturbing factors; and that the increase in rate of hydrogenation becomes abnormally large if other groups active towards nickel, but not open to hydrogenation, are also present. In other words, the nature of the unsaturated organic compound has a determining influence on the effect of the hydrogen concentration.

The above general results of our investigation may be illustrated by a few instances selected from the somewhat large number of compounds which we have investigated. The experimental data are given in the form of (i) the mean rates of absorption of hydrogen (litres per minute) over the same range of hydrogenation at varying pressures; and (ii) the ratios of these rates at the higher pressures to that at atmospheric pressure of hydrogen taken as unity. Observations were made at unit increments of pressure (atmospheres) from 1 to 4 or 5 atmospheres absolute.

#### I. NORMAL ACCELERATION WITH INCREASING PRESSURE (SIMPLE ETHYLENIC COMPOUNDS).

The data for ethyl cinnamate, ethyl linoleate and pinene may be taken as typical.

##### *Ethyl Cinnamate.*

As shown in Part V of this series of papers (*loc. cit.*), this ester is smoothly converted in the liquid state at 140° to 180° C. to ethyl  $\beta$ -phenylpropionate by passage of hydrogen in presence of nickel, the rate of absorption being practically constant for the greater part of the action.

176 grm. of pure ethyl cinnamate were hydrogenated at 140° C. in presence of 0.15 grm. of prepared nickel (0.085 per cent. Ni on the ester):—

Absolute pressures.	Mean rate of absorption.	Relative rates.
atm.	litres per minute.	
1	0.496	1.00
2	1.031	2.08
3	1.488	3.00
4	1.990	3.95

##### *Ethyl Linoleate.*

The ethyl linoleate employed was mixed with small proportions of ethyl oleate and ethyl esters of saturated fatty acids; these do not interfere with the course of hydrogenation which, as we have previously shown,\* is selective and may be divided, so far as the rate of hydrogenation is concerned, into

\* Part I, p. 142.

two phases: (i) an almost linear section of the absorption/time curve covering the action in which the esters less saturated than oleate are converted to a mixture of oleate and iso-oleates; and, after an abrupt fall in the rate of absorption, (ii) another sector of the curve corresponding to the production of stearate from the oleate and iso-oleates.

150 gramm. of ethyl linoleate (previously distilled in a vacuum) were hydrogenated in presence of 0.45 gramm. of nickel (0.3 per cent. Ni on the ester) at 180° C.

Absolute pressures.	Mean rates of absorption.	Relative rates.
atm.	litres per minute.	
	(i) Pre-oleate phase.	
1	0.8065	1.00
2	1.4495	1.80
3	2.2725	2.83
	(ii) Oleate phase.	
1	0.2293	1.00
2	0.4329	1.89
3	0.6665	2.91

### *Pinene.*

The hydrogenation of pinene was studied to examine the behaviour of a simple ethylenic hydrocarbon in the liquid state; Sabatier and Senderens\* have shown that it is converted smoothly into dihydropinene, the bridged-ring system remaining unaltered.

The hydrogenations were conducted at 160° C., at which temperature the vapour pressure of the pinene is approximately one atmosphere; consequently the effective pressure of hydrogen was one atmosphere less than the absolute pressure. The data obtained show that the acceleration in rate of hydrogenation was in simple proportion to the nett effective hydrogen pressure.

150 gramm. of pinene were treated with hydrogen in presence of 0.30 gramm. of nickel (0.2 per cent. Ni on the hydrocarbon) at 160° C. The absorption/time curve for pinene is of the approximately linear type.

Absolute pressures.	Partial pressure of hydrogen.	Mean rate of absorption.	Relative rates.
atm.		litres per minute.	
2	1	0.2595	1.00
3	2	0.5415	2.08
4	3	0.7956	3.05

## II. SUBNORMAL ACCELERATION WITH INCREASING PRESSURE (SIMPLE ETHYLENIC COMPOUNDS).

### *Ethyl Cinnamate.*

176 grm. of the ester were hydrogenated at 140° C. in presence respectively of 0.015, 0.030, and 0.150 grm. of prepared nickel.

	Mean rates of absorption.			Relative rates.		
	Litres per minute.					
Per cent. Ni in ester ...	0.008	0.017	0.085	0.008	0.017	0.085
Absolute pressures.						
1	0.048	0.115	0.496	1.00	1.00	1.00
2	0.063	0.222	1.031	1.32	1.93	2.08
3	0.065	0.260	1.488	1.35	2.26	3.00
4	0.069	0.294	1.990	1.43	2.53	3.95

### *Linseed Oil Glycerides.*

The following data were obtained with the refined glycerides of linseed oil hydrogenated at 180° C., and show the effect of pressure with varying concentrations of nickel over the two characteristic phases:—

- (i) Hydrogenation of linolenin and linolein to olein and iso-oleins.
- (ii) Hydrogenation of olein and iso-oleins to stearin.

#### (i) Pre-olein phase.

	Mean rates of absorption.			Relative rates.		
	Litres per minute.					
Per cent. Ni in oil .....	0.050	0.075	0.150	0.050	0.075	0.150
Absolute pressures. (Atm.).						
1	0.259	0.321	0.517	1.00	1.00	1.00
2	0.338	0.497	0.968	1.30	1.55	1.87
3	0.450	0.595	1.500	1.74	1.85	2.90
4	0.540	0.773	2.112	2.09	2.41	4.09

## (ii) Olein phase.

	Mean rates of absorption.		Relative rates.	
	Litres per minute.			
Per cent. Ni in oil .....	0·075	0·150	0·075	0·150
Absolute pressures. (Atm.).				
1	0·096	0·108	1·00	1·00
2	0·162	0·236	1·69	2·18
3	0·230	0·317	2·40	2·94

## III. ABNORMAL ACCELERATION WITH INCREASING PRESSURE (UNSATURATED ALCOHOLS AND ACIDS).

*Geraniol.*

Enklaar (*loc. cit.*) has shown that the products of vapour hydrogenation of geraniol are dimethyloctanol and dimethyloctane; we have found that, when this alcohol is hydrogenated in the liquid state, the formation of hydrocarbon only takes place to a very limited extent, and the action may be considered as practically normal.

100 grm. of geraniol were treated at 150° C. with hydrogen at varying pressure in presence of 0·50 grm. of prepared nickel.

Absolute pressure.	Mean rates of absorption.	Relative rates.
Atm.	litres per minute.	
1	0·127	1·00
3	0·521	4·10
4	0·720	5·67

*Terpineol.*

When hydrogenated over nickel in the state of vapour, terpineol yields exclusively the hydrocarbon hexahydrocymene, even at the low temperature of 125° C.\* but we have found that, operating with liquid terpineol at 150° C., direct addition of a molecule of hydrogen occurs with but little production of hydrocarbon, the action being thus more comparable with the reduction of liquid terpineol by means of palladium.†

\* Haller and Martine, 'Compt. Rend.,' vol. 140, p. 1303 (1905).

† Wallach, 'Annalen,' vol. 336, p. 37 (1904).

150 grm. of terpineol were hydrogenated at 150° C. in presence of 0.50 grm. nickel (0.33 per cent. Ni on the terpineol).

Absolute pressure.	Mean rates of absorption.	Relative rates.
Atm.	litres per minute.	
1	0.154	1.00
2	0.493	3.20
3	0.857	5.57
4	1.096	7.12
5	1.235	8.00

These results are characteristic for a number of unsaturated alcohols which we have studied, the relative rates being more abnormally high in the case of tertiary alcohols (terpineol and linaleol) than primary alcohols.

#### *Oleic Acid.*

200 grm. of highly refined oleic acid were hydrogenated at 180° C. in presence of 0.30 and 0.75 grm. of prepared nickel.

	Mean rates of absorption.		Relative rates.	
	Litres per minute.			
Per cent. Ni in acid.....	0.150	0.375	0.150	0.375
Absolute pressures. (Atm.).				
1	0.0471	0.2239	1.00	1.00
2	0.1332	0.5068	2.83	2.26
3	0.2300	0.8378	4.88	3.74
4	0.3073	1.1723	6.53	5.23

The abnormally high increases in rate of hydrogen absorption with increasing pressure may be contrasted with the direct proportionality of the figures for the olein phase of the hydrogenation of ethyl esters or glycerides of unsaturated fatty acids (pp. 244, 246); it is to be noted that the abnormality becomes somewhat less at relatively high concentrations of nickel.

#### IV. UNSATURATED ALDEHYDES AND KETONES.

These compounds are particularly interesting, in view of the results set out above, since, on the one hand, they contain an oxygenated group intermediate in constitution between the alcoholic and carboxylic radicles, and, on the other hand, this oxygenated group is, in contrast to the latter, one

that will combine with hydrogen in presence of nickel. They are thus more comparable, from the point of view of hydrogenation, with a di- or multi-ethenoid compound than with a combination of ethylenic linkage and a free hydroxyl or carboxyl radicle.

The effect of pressure on the rate of hydrogenation is, as a matter of fact, closely similar to that which is encountered with such multi-ethylenic substances as linolein or linolenin—an increase in rate which is in direct proportion, or else somewhat less than proportional, to the pressure.

The abnormal increases in rate of hydrogenation with increase of pressure which characterise both unsaturated alcohols and carboxylic acids do not appear in the case of the unsaturated aldehydes or ketones. The hydrogenation of citral and of carvone may be cited as typical examples.

#### *Citral.*

Brochet\* states that citral in the liquid state absorbs hydrogen readily in presence of nickel; we find that the addition of hydrogen is simple until saturation is approached, when side actions other than hydrogenation are apt to set in. The data now published therefore deal with the earlier part of the hydrogenation process, during which the simple hydrogenated citral is the only product of the action.

150 grm. of citral were hydrogenated at 150° C. in presence of 0.50 grm. nickel (0.33 per cent. Ni on the citral).

Absolute pressures.	Mean rate of absorption.	Relative rates.
Atm.	litres per minute.	
1	0.152	1.00
2	0.230	1.51
3	0.345	2.27
4	0.457	3.01

The relative increases in rate of hydrogenation are definitely subnormal, when compared with the speed of hydrogen absorption at atmospheric pressure; whilst the rates at 2, 3, and 4 atmospheres pressure, compared between themselves, are in the ratio 2.00 : 3.00 : 3.97, *i.e.*, in exactly direct proportion.

It is instructive to contrast these figures with the abnormally high ratios for the closely related alcohol geraniol (p. 246).

\* Brochet, 'Bull. Soc. Chim.' [4], vol. 13, p. 197 (1913).

*Carvone.*

Vavon\* found that in presence of platinum black carvone can be hydrogenated successively to carvotanacetone, tetrahydrocarvone (carvomenthone) and tetrahydrocarveol. We have obtained the same sequence of changes employing nickel with liquid carvone at 150° C.; the final reduction to tetrahydrocarveol is more difficult than the other stages, and we have compared the rates of hydrogenation at varying pressures only in the case of the saturation of the two ethylenic linkages of the ketone.

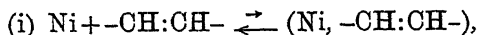
The data are quoted for ranges of hydrogen absorption representing approximately the addition of the first and second molecules of hydrogen per molecule of carvone, and within these respective ranges the ratios remained closely constant, a change from normal to somewhat subnormal values occurring at that part of the absorption.

150 gramm. of carvone were hydrogenated in presence of 0.50 gramm. of nickel (0.33 per cent. Ni on the carvone).

Absolute pressures.	Mean rates of absorption.		Relative rates.	
	1st mol. H <sub>2</sub> .	2nd mol. H <sub>2</sub> .	1st mol. H <sub>2</sub> .	2nd mol. H <sub>2</sub> .
Atm.				
1	0.406	0.399	1.00	1.00
2	0.803	0.673	1.98	1.69
3	1.282	1.058	3.16	2.65

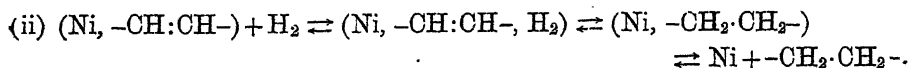
THEORETICAL CONCLUSIONS.

We have put forward the view† that the fundamental action in hydrogenation by nickel or other like catalyst is the balanced action



an extremely rapid equilibrium action, with the balance largely in favour of the unassociated components as indicated by the two arrows.

The slower action which is actually measured in work of this kind is, we consider, the interaction of this complex and hydrogen which is also associated with the nickel:—



This view of the process of hydrogenation receives fresh support from the data on the relation between pressure and rate of hydrogenation which we

\* Vavon, 'Comp. Rend.,' vol. 153, p. 68 (1911).

† Part I, p. 144.



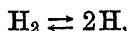
now put forward; the bearing of the latter may be considered in connection with the three classes into which they fall:—

1. *Simple Ethylenic Compounds—Simple Proportionality between Concentration of Hydrogen and Rate of Hydrogenation.*

The direct proportionality observed in the case of simple unsaturated compounds (except for extremely low concentrations of catalyst) can only mean that the rate of addition of hydrogen is connected directly with the concentration of the hydrogen as it is presented in the system, *i.e.*, in the molecular form— $H_2$ .

If the action were brought about by atomic hydrogen ( $-H$ ) it would appear that one of two alternatives must occur:—

(a) The measured action might be that of the dissociation of hydrogen in presence of nickel (*cf.* Sieverts, *loc. cit.*),



in which case the observed rate should vary as the square root of the hydrogen concentration and *moreover, should be independent of the constitution of the organic compound.*

(b) The measured action might be analogous to that given above (ii), and of the type:—



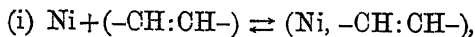
The increase in rate should then be proportional to the square of the increase in pressure, and could only appear in the observed simple proportion if both actions (a) and (b) were of the same velocity, an extreme coincidence which again excludes any possibility of varying rates of hydrogenation conditioned by the type of unsaturated compound—the factor which is most prominent in all our results.

It follows that the general results of this enquiry indicate that the speed of hydrogenation is directly proportional to the molecular concentration of the hydrogen, as expressed in our general equation (ii) above.

2. *Simple Ethylenic Compounds—Very Low Concentrations of Catalyst.*

We have shown that in this case the increase in rate of hydrogenation is subnormal, *i.e.*, is in less than direct proportion to the increase in pressure.

Now, considering the initial action



it is evident that the relatively low concentration of nickel (and corresponding relatively high concentration of unsaturated compound) will tend to displace

the equilibrium more in the direction of the complex ( $\text{Ni}, -\text{CH}:\text{CH}$ ) so that more of the nickel present will be monopolised by association with the unsaturated compound and consequently the hydrogen will have less nickel available for the preliminary association of hydrogen and nickel. Hence increased concentration of hydrogen cannot produce its full normal effect, the hydrogen and unsaturated compound competing, as it were, for the attention of the small amount of nickel present.

It must be borne in mind that the amount of hydrogen brought into contact with nickel and the organic liquid at any one moment is very small and is not comparable with the amount of unsaturated compound except quite towards the end of the action. For example, the apparatus which we have employed (using about 1 gram-molecule of compounds such as ethyl cinnamate or terpene derivatives) contains about 500 c.c. free gas-space (at N.T.P.), so that if the whole apparatus were filled with a uniform mixture of solid nickel, liquid and gas (which will not occur in practice) the amount of hydrogen present at  $0^\circ$  would be only about 0.022 gram-molecules and at  $150^\circ$  to  $180^\circ$  C. only about 0.013 gram-molecules at atmospheric pressure.

3. *Unsaturated Compounds Containing Groups which have Affinity for Nickel but are not open to Direct Hydrogenation.*

The abnormally rapid increase with the pressure in the rate of hydrogenation of such compounds as unsaturated alcohols and acids is equally explained by the above mechanism; in this instance, in addition to the hydrogenation actions represented by (i) and (ii) we have a third, independent action between nickel and the additional group, so that the catalyst is occupied with three potential factors, unsaturated linking, hydrogen and the new radicle which is not capable of hydrogenation. Increase in concentration of the hydrogen will promote the action (ii) between ethylenic linking, nickel and hydrogen, but will have no direct influence on the association between nickel and the hydroxyl or carboxylic group. Consequently, and especially if the affinity between nickel and the other radicle is stronger than that between the metal and the unsaturated residue, the rate at which the action (ii) proceeds will increase abnormally with the pressure.

This behaviour may very possibly, also, be related to the general function of adsorption as defined by the work of Langmuir\* and of Hardy.†

If, granting the presence of a suitable adsorbent surface, simple adsorption is conditioned by the relative affinities of various groups, the results which

\* 'J. Amer. Chem. Soc.,' vol. 38, p. 2221 (1916); vol. 39, p. 1848 (1917); vol. 40, p. 1361 (1918).

† 'Roy. Soc. Proc.,' A, vol. 86, p. 631 (1912); A, vol. 88, p. 303 (1913).

we have observed would follow when there is present at the surface (or forming the surface) a material which can induce actual chemical action between the less strongly attracted (adsorbed) of two or more radicles and an independently adsorbed substance (hydrogen).

We have used the term adsorption here in the same sense as that in which Langmuir has defined it, namely, as a phenomenon which is caused by the same forces as are operative in any other chemical action; we regard "adsorption," if it is not absolutely identical with what we have referred to as "unstable intermediate compounds," as being the immediate precursor of the latter.

The investigation of the relation between hydrogen pressure and hydrogen absorption by unsaturated compounds in presence of nickel therefore has confirmed our former views of the primary dependence of the whole process upon the relations and affinities subsisting between the catalyst and the unsaturated organic compound.

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### *On "Light Body" Hydrophones and the Directional Properties of Microphones.*

By A. B. WOOD, D.Sc., F.Inst.P., and F. B. YOUNG, B.A., D.Sc., F.Inst.P.

(Communicated by Sir W. Bragg, F.R.S. Received March 10, 1921.)

The work to be described was carried out in August–September, 1916, and is now published with the permission of the Admiralty.

#### *1. Ellipsoidal Directional Hydrophones.*

Prof. W. H. Bragg in 1916 suggested a simple form of directional hydrophone, consisting of an elongated body of rigid but light construction, in which was mounted a carbon granule microphone of the "button" type. The principle of action of this body was expected to be as follows:—If a body floats freely, wholly or partly submerged, in water through which sound waves (or other waves) are passing, it oscillates with the water and with the same amplitude as the water, provided its dimensions are small compared with the wave-length. This follows from the fact that both the mass of the body and the forces which act on it are the same as in the case of the water which it has displaced.

If, however, the mass of the body is less than that of the water which it

displaces (in which case, of course, constraint must be used to keep it down), the motion of the body is greater than that of the water, provided that the constraints do not interfere with the vibratory motion, and *vice versa*. Since the body now moves with respect to the water, the amplitude of its motion will, from hydrodynamical considerations, depend upon the shape of the body. If, for example, the body is ellipsoidal, its motion will be greatest when the greatest axis coincides with the direction of the wave. The response of the enclosed microphone will vary, therefore, with the orientation of the ellipsoid; hence the "light body" will constitute a directional hydrophone.

Prof. Lamb supplied the following data for a prolate ellipsoid. The numbers give the "inertia coefficient," or the ratio of the water-load to the mass of water displaced by the body, for different values of the ratio of the length,  $c$ , to the greatest breadth,  $a$ . The numbers are given for two orientations of the body:—(i) the "end-on" position, in which  $c$  is inclined at  $0^\circ$  to the direction of the propagation of the sound; (ii) the "broadside-on" position, in which  $c$  is inclined at  $90^\circ$  to the direction of the propagation.

Table I.

$c/a$ .	Inertia coefficient ( $\beta$ ).	
	End-on ( $\beta_1$ ).	Broadside-on ( $\beta_2$ ).
1	0.5	0.5
1.5	0.305	0.621
2.0	0.209	0.702
2.5	0.156	0.763
3.0	0.122	0.803
4.0	0.082	0.860
5.0	0.059	0.895
6.0	0.045	0.918
7.0	0.036	0.933
8.0	0.029	0.945
9.0	0.024	0.954
10.0	0.021	0.960

Let  $M$  be the mass of the body,  $M'$  that of the fluid displaced by it, and  $\beta$  the inertia coefficient. Then, if the length of the sound waves is considerable compared with  $c$  or  $a$  respectively and the body is immersed and free to move,

$$\frac{\text{amplitude of body}}{\text{amplitude of sound waves}} = \frac{(1+\beta)M'}{M+\beta M'} = \frac{1+\beta}{\rho+\beta}$$

where  $\rho$  is the density of the body.

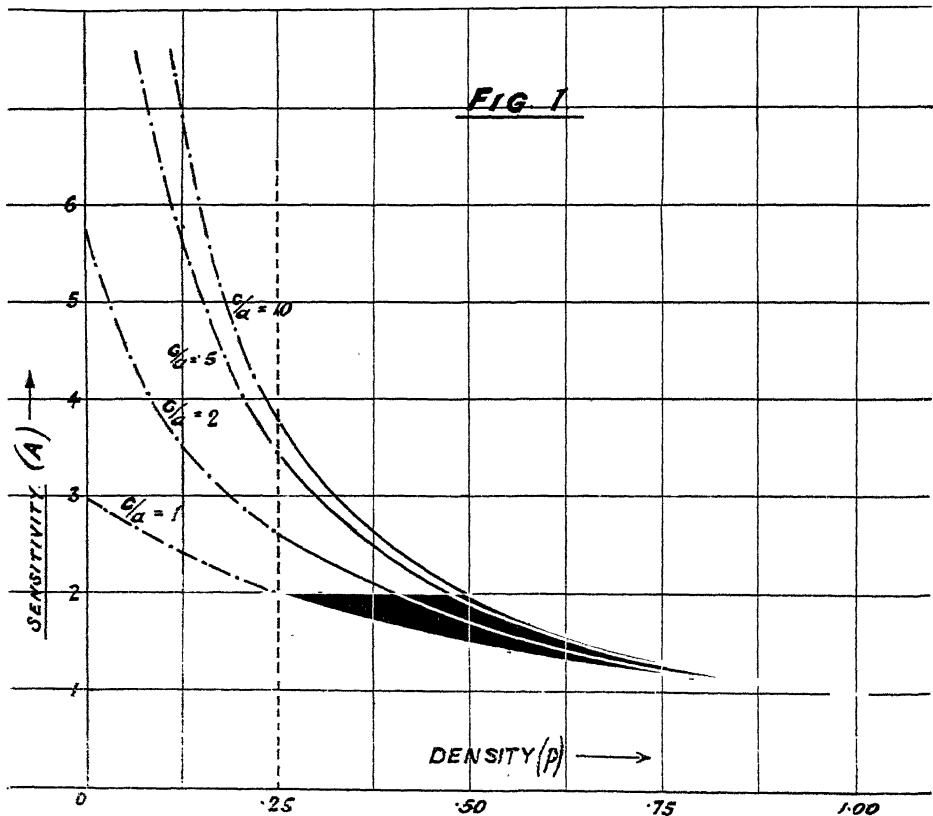
It is apparent that the relative amplitude,  $A_0$ , of the body in the end-on

position is greater than its relative amplitude,  $A_{90}$ , in the broadside-on position. The ratio,  $A_0/A_{90}$ , may be termed the direction ratio, and its magnitude is a measure of the efficiency of the body considered as a direction finder.

$$A_0/A_{90} = \frac{1+\beta_1}{\rho+\beta_1} \bigg/ \frac{1+\beta_2}{\rho+\beta_2}.$$

$A_0$  is the ratio of the maximum amplitude of the body to the amplitude of the water, and may therefore be termed the "coefficient of sensitivity." The sensitivity coefficient and direction-ratio are both of practical significance in the hydrophone; and the relations between these and the shape and density of the ellipsoidal body are shown graphically in figs. 1 and 2, for densities less than 1.

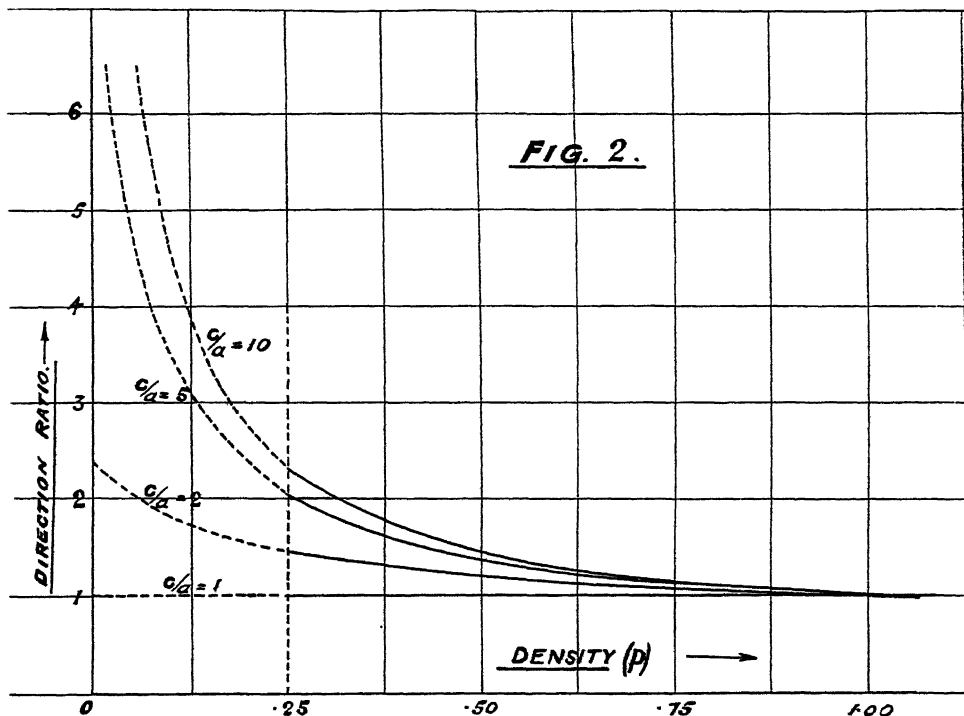
In fig. 1 the sensitivity is seen to increase as the density decreases, reaching a theoretical maximum when  $\rho = 0$ . The practical maximum is, however, reached when the limit of lightness consistent with rigidity is attained, since the theory assumes that the body moves without deformation of shape. This limit is, of course, indeterminate, but is probably not lower



than 0.25. Thus, though for  $c/a = 10$  and  $\rho = 0$ ,  $A_0 = 46.6$ ; if  $\rho$  has the minimum practical value of 0.25,  $A_0 = 3.8$ .

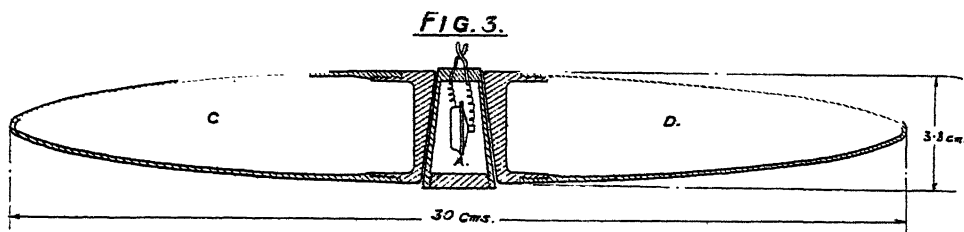
From fig. 1 it is also seen that for any given value of  $\rho$  less than 1 the sensitivity increases with  $c/a$ , but at a rapidly diminishing rate, and in practice there is little advantage in taking a higher value for  $c/a$  than 5 or 6.

In fig. 2 is plotted the direction-ratio with density for various values of  $c/a$ . The curves have the same general character as in fig. 1, and the same



general remarks apply. Though for  $c/a = 10$  the directional ratio has the high theoretical maximum of about 24, it is only 2.3 when  $\rho = 0.25$ .

A glass ellipsoidal body was prepared by Sir E. Rutherford similar in general form to fig. 3. It consisted of two portions, fitting together with a ground-glass joint, which permitted of the insertion of a button microphone,



which was mounted with its axis parallel to the major axis of the body on a small wooden block cemented to the glass. The leads of the microphone were carried through the glass by sealed platinum wires. The external dimensions were  $c = 32.0$  cm.,  $a = 4.5$  cm.; and the mean density,  $\rho$ , was 0.3. Hence  $c/\alpha = 7.1$ , and the direction ratio is given by

$$A_0/A_{90} = \frac{1+0.035}{0.3+0.035} \bigg/ \frac{1+0.934}{0.3+0.934} = 2 \text{ (nearly).}$$

For practical test the ellipsoid was supported in a wire frame with twine ties, so that it might oscillate with a minimum of constraint, and it was immersed in a tank of water which contained also an electrical buzzer. The leads were connected in series with a battery and the primary of a telephone transformer in the customary manner. It was found that the microphone responded well to the sound waves, and on rotation about a vertical axis the body proved to have very marked directional properties. The direction ratio was, in fact, far greater than the calculated value, 2; it was estimated to be from 20 to 40.

## 2. *Directional Properties of Microphones.*

The discrepancy between the theoretical and the experimental direction ratio led to an examination of the button microphone. The following simple tests were made:—

(a) A button microphone was mounted with soft wax on a prong of a tuning fork, the other prong of which was also equally loaded. The microphone having been connected into a telephone circuit, the fork was thrown into vibration. The test was made with the axis of the microphone diaphragm, (i) parallel to the plane of vibration, (ii) at right angles to that plane. It was observed that the response was much louder in case (i) than in case (ii).

(b) A button microphone was mounted on an ebonite button cemented to the side of a small round-bottomed flask, the leads being passed through the cork stopper. This when immersed upright in the tank constituted a rough "light body" hydrophone which, from considerations of symmetry, should have been non-directional. It was observed, however, that as the flask was rotated about a vertical axis the response of the microphone varied very markedly, the sound heard in the telephone receivers being at a maximum when the microphone axis was parallel to the direction of the propagation and almost *nil* when the axis was at right angles to that direction.

It was thus apparent that the microphone has very pronounced directional properties, and that the glass ellipsoid owed its directional properties largely to the microphone.

An attempt was made to measure the direction-ratio,  $A_0/A_{90}$ ,  $A_0$  and  $A_{90}$

in this case being the amplitudes of the oscillating current when the axis of the microphone was parallel and at right angles respectively to the line of propagation of the sound. The comparison between  $A_0$  and  $A_{90}$  was made by shunting down the maximum response to equality with the minimum. The test was repeated with various specimens of microphones mounted in flasks of various sizes. It was found that the ratio varied considerably, even with the same microphone and flask, but reached values as high as 40 or 50. The method of mounting was varied, the microphone being sometimes cemented to the ebonite button by its case and sometimes screwed to the button by its diaphragm. No definite difference in the direction ratio depending upon the method of mounting was detected, the only desideratum for a high value being that the attachment should be rigid.

A number of flasks of various sizes were tested with the object of determining to what extent the sensitivity was actually affected by the mean density. One flask being retained as standard, the other flasks were fitted in turn with the same microphone, and the sensitivities of the flasks were compared directly with the standard. No very consistent results were obtained. Flasks having capacities respectively of 32 oz. (density = 0.10), 12 oz. (density = 0.16), and 4 oz. (density = 0.25) appeared to be of about equal sensitivity, whilst a flask of 22 oz. capacity (density = 0.15) was more sensitive than any. Smaller flasks of about 1 oz. or  $\frac{1}{2}$  oz. capacity were, however, distinctly less sensitive, probably on account of the damping effects of the leads. The directional properties of the larger flasks seemed less certain than those of the smaller, suggesting that the larger flasks were lacking in rigidity, and it was from these experiments that the conclusion was drawn that the density cannot be reduced with advantage below about 0.25.

It may be mentioned that no definite indication was obtained of dissymmetry between the two maxima due to the unsymmetrical mounting of the microphone. It was necessary, however, to observe great care in maintaining the axis of the flask vertical, as the microphone proved to be very sensitive to changes in the inclination of its diaphragm.

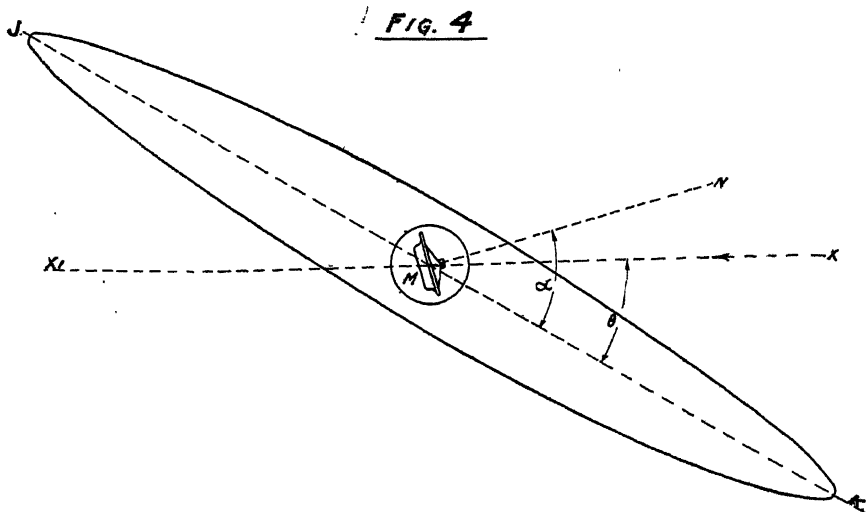
### *3. Verification of the Ellipsoidal Principle.*

Though the directional properties of the microphone prevented direct verification of the principle of the elongated light body, verification was obtained indirectly in the following manner:—A hollow ellipsoid was constructed of ebonite, 30 cm. long and 3.8 cm. broad (fig. 3). Into the central section, A, was tightly fitted a hollow conical plug, which enclosed the microphone. The end sections, C and D, could be unscrewed from A and, if



desired, weighted with paraffin wax or other material. The edge of the socket in A was graduated in degrees, so that the plug carrying the microphone could be rotated through known angles. The ellipsoid was supported like the earlier glass instrument in the tank.

The microphone plug was rotated so that its axis, MN (fig. 4), made a certain angle,  $\alpha$ , with the major axis, JK, of the ellipsoid. Then, by rotating



the whole ellipsoid, the position was found for which the response of the microphone was a maximum and the angle,  $\theta$ , made by JK with the direction, XX<sub>1</sub>, of propagation of the sound was determined. In practice the body was rotated in either direction in turn until the two positions of the minimum response were reached, and the position of the maximum was then assumed to lie midway between these, this plan being adopted owing to the far greater accuracy with which the minima could be determined than the maxima. The angle  $\theta$  was determined in this way for various values of  $\alpha$ .

The mean density of the ellipsoid as first employed was found to be 0.42. A second set of readings was made at a mean density of 1.0, the body being suitably loaded. A further series of readings at a still higher density was abandoned, owing to the low sensitivity of the instrument and the indefiniteness of the maxima. The readings are tabulated in Table II.

It will be observed that the readings were indefinite for  $\rho = 1$ ,  $\alpha = 60^\circ$ , whilst for  $\rho = 1$ ,  $\alpha = 75^\circ$  the minima were so vague that the readings are omitted. It is probable that the method of loading up the body affected its rigidity, leading to disturbing vibrations within the body itself. When the load was further increased these disturbances became so serious as to make observations impracticable.

Table II.

$\alpha$ .	$\theta$ (mean value).		Tan $\alpha$ /tan $\theta$ .		$A_0/A_{90}$ (from Lamb's figures).	
	$\rho = 0.42$ .	$\rho = 1.00$ .	$\rho = 0.42$ .	$\rho = 1.00$ .	$\rho = 0.42$ .	$\rho = 1.00$ .
0	0	0	—	—	1.60	1
30	-18	-30	(1.8)	1		
45	-33	-45	1.54	1		
60	-48	-55 -70	1.68	—		
75	-68	?	1.50	?		
90	-90	-90	—	—		
Mean =			1.56	1.0		

The observations indicate that when  $\rho = 1$  the directional properties of the instrument reside entirely in the microphone, as theory would indicate. When  $\rho = 0.42$ , though the influence of the microphone still predominates, the readings show clearly the effect of the ellipsoidal form.

The data given by Prof. Lamb may be tested as follows:—As before, let  $A_0$  and  $A_{90}$  be the respective amplitudes of the ellipsoid (in terms of the amplitude of the water taken as unity) for the positions  $\theta = 0^\circ$  and  $\theta = 90^\circ$ . Let JK be rotated through any angle  $\theta$ . Then the amplitude of the sound waves may be resolved into rectangular components acting along JK and at right angles to JK respectively; the corresponding component amplitudes of the ellipsoid will be  $A_0 \cos \theta$  and  $A_{90} \sin \theta$ .

Again, resolving each of these components in directions parallel to and at right angles to the axis of the microphone, the amplitude  $A_m$  in the former direction is given by

$$A_m = A_0 \cos \theta \cos \alpha + A_{90} \sin \theta \sin \alpha.$$

If now we assume that the microphone is practically insensitive except to vibrations parallel to its axis, MN, then the response of the microphone will be proportional to  $A_m$ . Hence the condition that the response shall be a maximum is that  $\frac{dA_m}{d\theta} = 0$ , i.e., that  $\frac{A_0}{A_{90}} = \frac{\tan \alpha}{\tan \theta}$ .

Thus the ratio  $A_0/A_{90}$  for the ellipsoid should be calculable from the experimental values of  $\alpha$  and  $\theta$ . The values of  $\tan \alpha/\tan \theta$  are given in Table II.

From Lamb's data, if  $\rho = 0.42$  and  $c/a = 30/3.8 = 7.9$ ,

$$A_0/A_{90} = \frac{1+0.030}{0.42+0.030} \bigg/ \frac{1+0.944}{0.42+0.944} = 1.6.$$

This value is in very fair agreement with the value of  $\tan \alpha / \tan \theta$ , except in the case where  $\alpha = 30^\circ$ , when the angle  $\theta$  to be determined acoustically is small and is liable to a comparatively big proportionate error in the setting of the apparatus. If  $\rho = 1.00$ , then  $A_0/A_{90} = 1$  for all values of  $c/\alpha$ . This is also in agreement with the experimental results. It was observed that as the ellipsoid was loaded up the response of the microphone became feebler, as theory would predict. No quantitative data, however, were obtained.

#### 4. "*Light Body*" *Directional Hydrophones.*

The salient facts in regard to the production of a practical "light body" directional hydrophone may be summarised as follows:—

(i) Assuming the minimum density consistent with rigidity to be 0.25, the sensitivity coefficient may vary with the elongation from 2.0 for  $c/\alpha = 1$  to 3.8 for  $c/\alpha = 10$ . The variation is less for higher densities.

(ii) The maximum direction ratio due to elongation is about 2.3 under practical conditions; this is negligible compared with the direction ratio obtainable from a well mounted microphone.

Hence it appears that little advantage is gained from adhering to the ellipsoidal form, whilst a sphere has the advantages of greater compactness and greater rigidity.

Probably from the acoustic point of view no more suitable material than glass could be employed were it not so fragile. Ebonite has, however, been found to give good results, the shell being turned as two hemispheres, which are carefully fitted and cemented together. Prof. A. L. Hughes employed with equally good results spheres of paraffin wax, cast round a light central brass box containing the microphone. In the case of the ebonite instruments various sizes were tested; the experiments led to the conclusion that no increase of efficiency was obtainable by increasing the diameter of the sphere beyond about 2 inches. Elongated bodies containing rigidly mounted microphones have been employed by various experimenters with some success as towed hydrophones.

The "light body" hydrophone is inferior in sensitivity to other types, and in practice would need slight amplification. But owing to the well-known fact that a carbon granule microphone is never entirely free from crepitation, which is amplified together with the vibrations to be transmitted, the use of an amplifier with such a microphone is open to objection. A small ebonite spherical hydrophone 1 inch in diameter, however, proved invaluable as an exploring instrument in certain investigations made by the writers and described elsewhere.

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*On the Acoustic Disturbances Produced by Small Bodies in Plane Waves Transmitted through Water, with special Reference to the Single-plate Direction Finder.*

By A. B. WOOD, D.Sc., F.Inst.P., and F. B. YOUNG, B.A., D.Sc., F.Inst.P.

(Communicated by Sir W. Bragg, F.R.S. Received March 10, 1921.)

1. INTRODUCTORY.

The experiments to be described were carried out for the Board of Invention and Research, under the direction of Sir William Bragg, between October 1916 and February 1917, on the Cullaloe Reservoir, near Aberdour, Fifeshire, and are now published with the permission of the Admiralty.

A form of directional hydrophone has already been described by Sir William Bragg. It consists of a metal diaphragm, A, about four inches in diameter, mounted in a heavy ring, B, and open to the water on both sides (*vide* Chart 9). In the centre of the diaphragm is a small metal box, C, carrying a carbon granule microphone of the button type. The microphone is connected into an ordinary telephone circuit. If the instrument is rotated about a vertical diameter in water through which sound waves are passing the sound heard in the receivers passes through a number of maxima and minima. When the diaphragm is turned "edge-on" to the source of sound it is obvious that the pressure pulses will reach the two faces of the diaphragm symmetrically and the diaphragm will fail to vibrate. As, however, either face is turned toward the source this symmetry ceases to exist and the diaphragm is thrown into vibration, which reaches a maximum amplitude when the instrument is "broad-side" on to the source. The instrument, therefore, indicates the line of propagation of the sound, but owing to the existence of two positions of maximum or minimum its indications are ambiguous as regards the sense of direction.

Attempts were made to remove this ambiguity by mounting a small screen or baffle plate opposite one face of the diaphragm. Discs of lead, iron or wood appeared to be without influence, but a wooden disc covered with sheet lead actually gave the desired result, the response of the microphone being less when the shielded face was turned toward the source than when the exposed face was so directed (*vide* Section 3).

Though the lead-wood baffle acted as though it were casting an acoustic shadow upon the diaphragm, the production of a shadow in the optical sense would be impossible, since the diameter of the disc was small compared with the wave-length of the sound; the wave-length in water for a frequency of

1000  $\sim$ /sec. is about 5 feet whilst the diameter of the disc was 10 inches

only. Calculation of the disturbances produced by small screens is possible only in certain simple cases, and the experiments to be described were undertaken with the object of elucidating the essential conditions of baffle action.

Work in a laboratory tank was rendered impossible by the interference of reflections from the sides. The investigation was, therefore, carried out on a raft moored on the Cullaloe Reservoir.

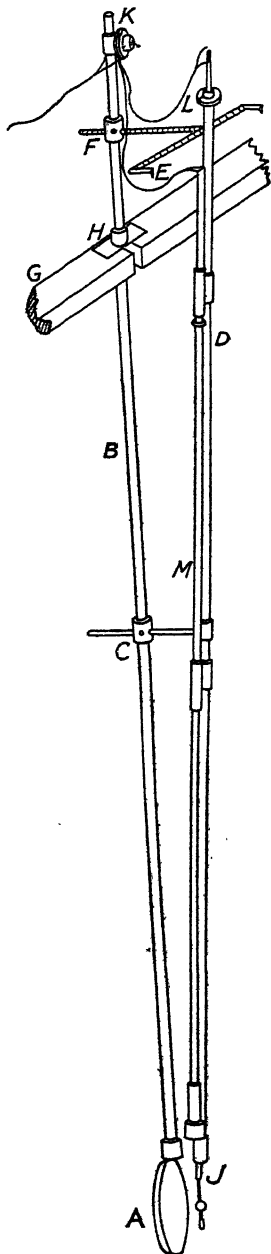


FIG. 1.

## 2. EXPLORATION OF THE ACOUSTIC FIELDS IN THE NEIGHBOURHOOD OF SMALL SCREENS IMMERSED IN WATER.

The acoustic fields were charted around a variety of small discs placed in the path of a train of (approximately) plane sound waves propagated through water. The preparation of the charts involved the determination at a series of points of—

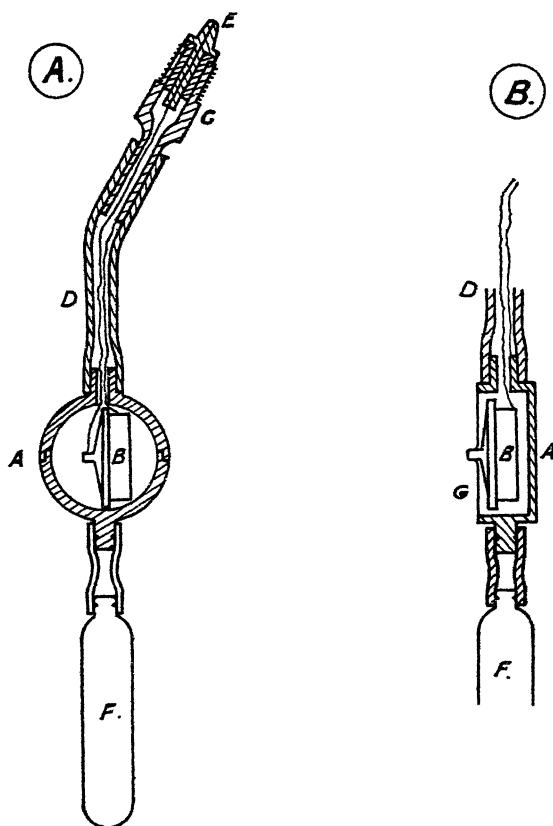
- (i) the direction of oscillation of the water particles.
- (ii) the amplitude of the displacement of the particles.
- (iii) the amplitude of the pressure oscillations.

### (a) *Apparatus.*

The exploring apparatus is shown in fig. 1. The screen, A, is suspended from an iron tube, B, about 11 feet in length. A light steel tube, D, is so mounted near its centre point as to be free to rock in any direction but not to rotate. The exploring instruments are carried at the lower end of D, whilst the upper end travels along a graduated guide bar, E, the graduated supporting rod of which slides in a boss, F. By means of

E and F the positions of the exploring instruments with respect to the disc could be determined.

The "Displacement Explorer" (fig. 2A), is a small "light body" hydrophone,\* consisting of a hollow ebonite sphere, A, about 1 inch in diameter, in which an A.T.M. button microphone, B, is rigidly mounted by its back. It is suspended by the rubber tubing, D, and held in a vertical position by the brass weight, F. As elsewhere explained (*loc. cit.*), this instrument acts as a directional



VELOCITY EXPLORER.

PRESSURE EXPLORER.

FIG. 2.

hydrophone, the microphone responding readily to sound waves which travel in a direction parallel to its axis, but very slightly to those whose direction is parallel to its diaphragm. The flexible suspension is rendered necessary by the sensitiveness of the microphone to slight changes of inclination and also

\* *Vide* the preceding paper, "On 'Light Body' Hydrophones and the Directional Properties of Microphones."

serves the purpose of acoustic insulation. The instrument is attached to a light rotatable tube, J, passing up through D, and indicating the orientation of the sphere on a dial, L. (see fig. 1).

The "Pressure Explorer" (fig. 2B) is a shallow brass cylindrical box, A, about 1 inch in diameter, the lid of which consists of a thin diaphragm, G, on which is mounted a microphone, B. This is attached to tube M (in fig. 1).

By means of tubes M and J the explorers can be retracted at will, so that only one at a time is in operation.

Fig. 3 shows how the explorers are connected one at a time through a switch, K, into a telephone circuit. For purposes of quantitative measurements the receivers, P<sub>1</sub>, P<sub>2</sub>, are connected through a potentiometer rheostat, Q, the switch, S, serving to tap off either the fixed length, RT, or the adjustable portion,

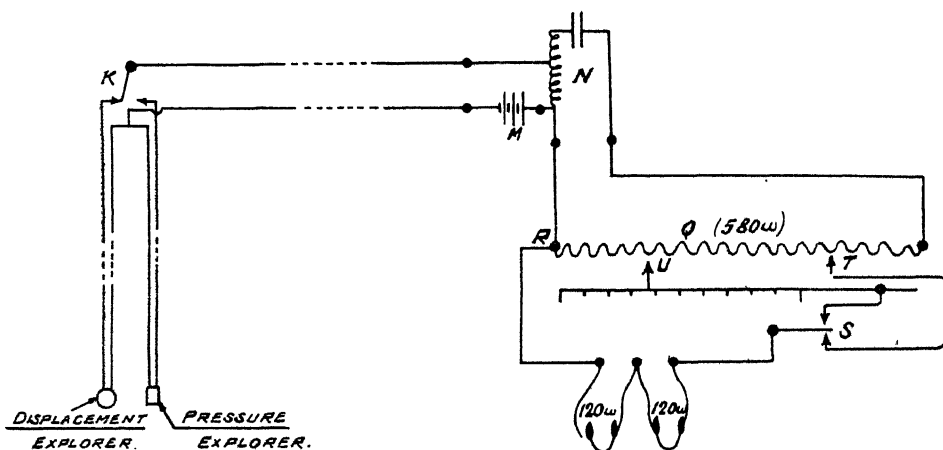


FIG. 3.

RU, at will. If the intensities at two points in the field are to be compared the explorer is moved to and fro between those points whilst S is simultaneously switched over. Contact U is adjusted by trial till the sounds in the telephones have equal intensities. The resistances are so arranged that the ratio of the amplitudes at the two points is given by the inverse ratio of the lengths of the rheostat tapped off.

Fig. 4 shows the general dispositions. The exploring apparatus is supported in the well, A, of a raft so that the disc and explorers are immersed to a depth of about 8 feet. The walls of the well, which dip into the water, ensure calm water immediately round the apparatus. A light wooden hut serves both to shelter the observers from the weather and to facilitate listening by screening them from the wind. The sources of sound are

suspended at the end of a light boom extending from the front of the hut. These are two in number :—

- (i) An electric “buzzer” enclosed in a watertight case and giving a

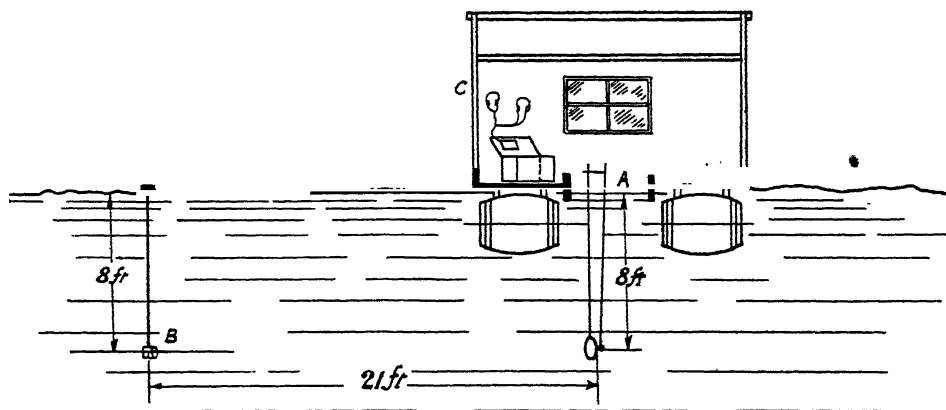


FIG. 4.

continuous musical sound, whose principal component had a frequency of 580~/sec., though components both an octave below and an octave above this were distinguishable.

- (ii) A “tapper,” consisting of an electric bell mechanism enclosed in a case, against which the hammer strikes. The sound produced was chiefly of the nature of a low rumble, though higher frequencies were present. No predominant frequency, however, could be observed.

The raft was moored in about 25 feet of water and about 70 yards from the nearest bank, so that echoes from the bank would be extremely feeble in comparison with the sound received directly from the source.

#### (b) *Method of Experiment.*

A point-to-point exploration was made by each of the explorers in turn in the horizontal plane passing through the centre of the screen, the movements of the end of the lever, D, being assumed to be practically confined to this plane. The direction of the oscillations at a given point was first determined by rotation of the displacement explorer to the position of minimum response, this position being taken in preference to that of maximum response, as being more sharply defined.

The amplitude of the water particles was compared with that at a reference point 10 inches from the axis of the screen by means of the potentiometer employed as explained in (a). Since the reference point was always taken in the same parallel, it was necessary subsequently to compare



directly the various reference points, and, if necessary, to adjust the readings.

The amplitude of the pressure oscillations was determined in the same manner as the displacement amplitude, the pressure explorer being substituted for the displacement explorer.

(c) *Treatment of Results, Limits of Error, etc.*

In drawing out the charts, the average readings have been taken for the points' symmetrical about the axis when those readings clearly pointed to a symmetrical arrangement. In this way slight errors in the initial adjustment, etc., were eliminated. In other cases the readings have been plotted in full.

In addition to the quantitative observations already referred to, an attempt has been made to report qualitative variations where they were sufficiently defined. These are explained in Section 2 *d*.

Under favourable listening conditions, and when the oscillations were rectilinear, the direction could be determined to within about 5°. The accuracy of the readings was naturally diminished in cases of confused direction (*e.g.*, Chart 3), and cases occurred in which no variation with rotation of the displacement explorer could be observed.

Tests of the observers showed that, under favourable listening conditions it was possible to distinguish a difference of 10 per cent. between two sounds of the same quality. The accuracy of the observations was, however, diminished somewhat during windy weather. The season of the year was in this respect rather unfavourable, though it may be mentioned that many of the charts were made during a prolonged frost, when for five weeks the frozen surface of the reservoir rendered listening conditions ideal. The most serious obstacle to accurate intensity determinations was the occasional occurrence of qualitative differences in the sounds to be compared, due apparently to the differences in the renderings of the harmonics. In such cases divergencies of opinion between the observers often occurred, and it was noticeable that one appeared relatively more sensitive than the other to sounds of a higher general pitch.

In view of the above sources of error, the quantitative observations should be regarded as giving the general character of the acoustic field rather than as affording precise data. At the same time, it should be stated that, where observations were repeated on different days, they were generally in good agreement.

(d) *Symbols employed in Charts.*

(i) *Direction*.—A stroke (*a*) denotes the direction of oscillation of a water particle at the centre point of the stroke. The simple stroke implies

that the minima are well marked, indicating that the oscillations are sensibly rectilinear.

A dotted stroke (*b*) indicates that the minima are not clearly marked, and the symbols (*c*), (*d*), and (*e*) represent increasing blurring of the minima, the last symbol (*e*) denoting that no variation in intensity with rotation of the explorer is distinguishable. The water particles may be regarded as describing elliptical paths which in (*e*) approximate to circles.



It frequently happens that as the explorer is rotated marked changes of quality occur together with, or instead of, changes of intensity, the effect being such as to suggest that two distinct trains of waves are passing through the given point along paths roughly at right angles to one another. This effect is represented by the symbols (*f*), (*g*), (*h*), progressively indicating increasing loudness of the minima. When the two components are sensibly equal in intensity the two lines are dotted (*h*), since in this case their directions can rarely be determined with accuracy.



The fine lines are drawn through regions, where the directional indications are definite, to indicate the acoustic "rays." Where the directional indications are confused and complex, these lines are omitted. The lines are intended to assist in gaining a comprehensive view of the chart rather than as an analysis of the acoustic conditions.

(ii) *Amplitude Readings*.—The relative amplitudes are represented by numbers. The amplitude at the point in the chart where the sound distribution is considered to be least disturbed by the disc is taken as the standard and given the value 10. The point of reference is denoted by a ring, thus (10). Numbers representing displacement are printed to the right of the stroke indicating direction; those representing pressure amplitudes are printed to the left of the stroke and are turned through 90°.

(iii) *Corresponding Points on Opposite Faces*.—If the faces of the disc are similar, the transition from the side near the source to the side remote from it was affected by rotating the whole of the apparatus, including the disc, through 180°, so that the exploration was carried out opposite the same face throughout. This is indicated in the diagram by the letters  $a_1$ ,  $b_1$ ,  $a_2$ ,  $b_2$ , which denote the successive positions of the face  $ab$ .

#### (e) *Notes on Charts.*

It will be observed that the principal phenomena exhibited by the charts are of two distinct types, according as the acoustic field is produced around (i) a solid body, (ii) a hollow body. •

(i) *Solid Bodies*.—The charts of the lead disc are given as typical of fields procured by solid bodies, which exhibit the following characteristics:—

- (i) The lines of direction bend round the edges of the disc. At the same time a considerable portion of the sound energy is transmitted directly through it. The direction is clearly defined at every point.
- (ii) There is in general a diminution in the displacement amplitude near either face of the disc.
- (iii) No variation in the pressure amplitude is observable. This implies that any such variation from the primary amplitude must be less than 10 per cent.

A small dense solid obstacle such as the lead discs in Charts 1 and 2 may be regarded as acting the part of (i) a simple source, due to its great rigidity relatively to that of the water; (ii) a double source, due to its greater density and the lesser mobility resulting therefrom. Considered as a simple source, it virtually expands and contracts relatively to the adjacent

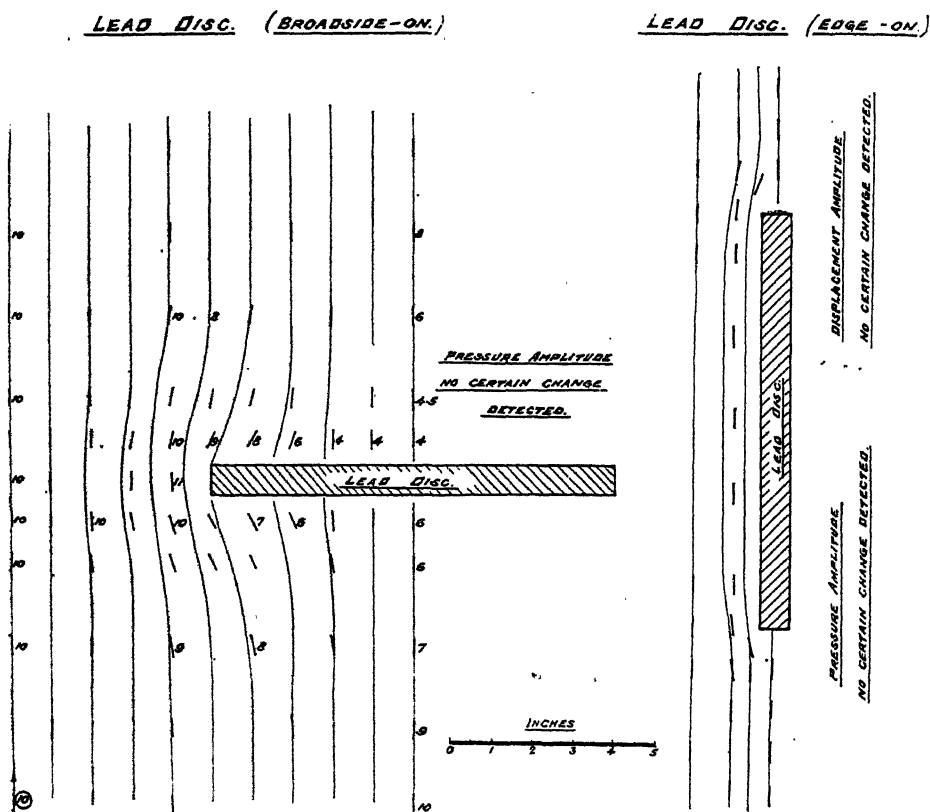
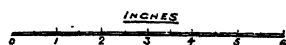


CHART I.

water as that water contracts and expands, thus giving rise to secondary vibrations in the same phase as the primary. Considered as a double source, it virtually oscillates in opposite phase to the adjacent water, tending to give rise at the near surface (*i.e.*, the surface facing the source) to vibrations in the same pressure phase as the primary waves, and at the remote surface to waves in the opposite pressure phase. In the latter case, however, if the dimensions of the disc are small compared with the wavelength, the motion results principally in lateral oscillations of the water round the edges of the disc. The form of the "stream lines" in the charts is adequately accounted for if they are considered to represent the resultant of the primary oscillations and the secondary lateral oscillations. The absence of any appreciable effect due to the rigidity of the disc is of course to be expected from its small thickness compared with the length of the sound waves.

LEAD DISC. (INCLINED AT 45°)



PRESSURE AMPLITUDES—  
NO VARIATION DETECTED.

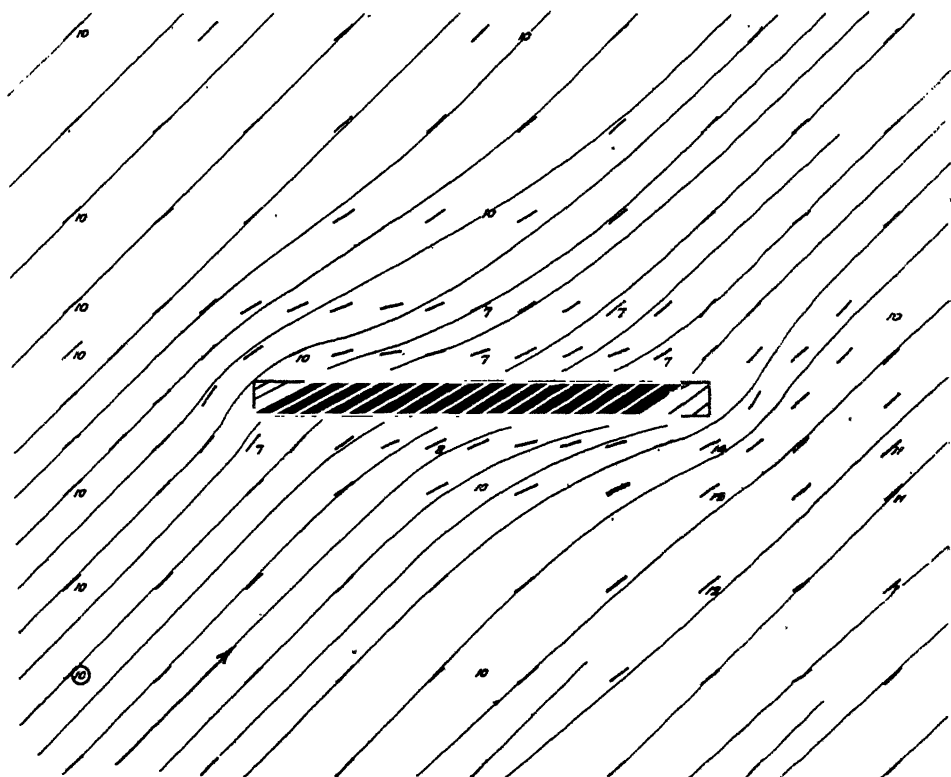


CHART 2.



OILED-SILK-AIR DISC. (Edge on Position.)

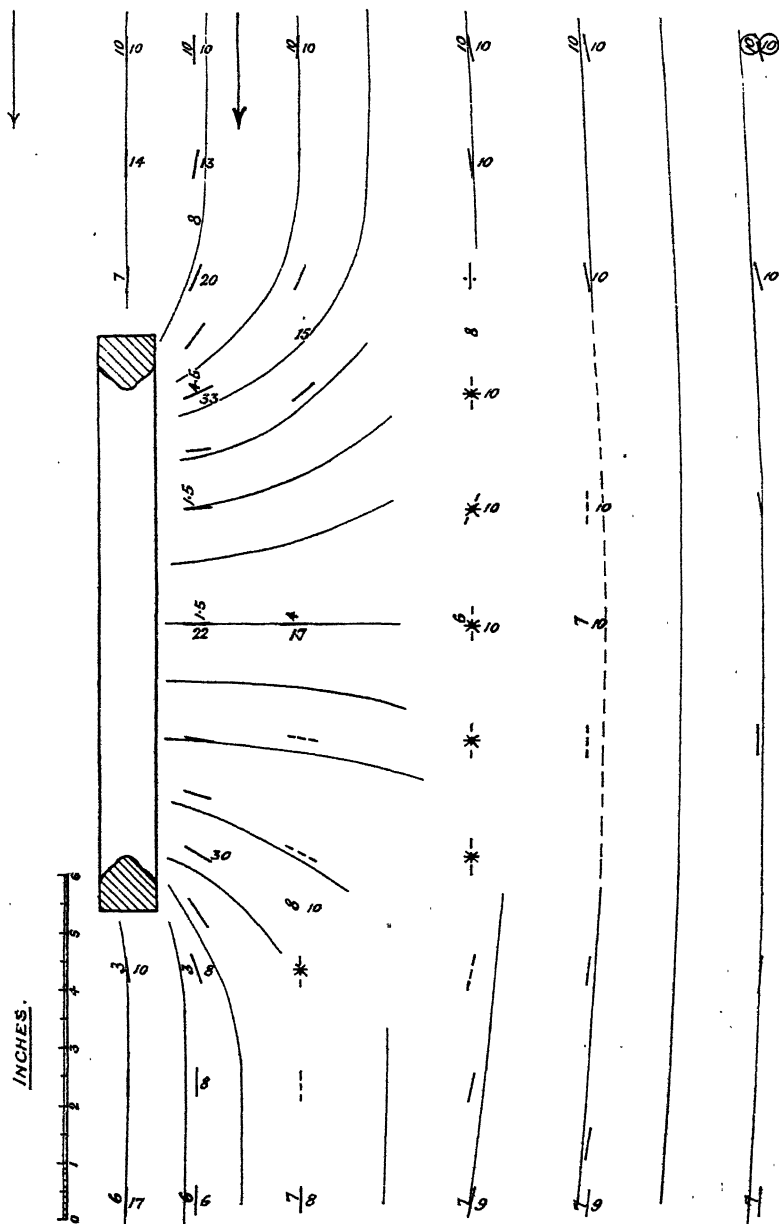


CHART 4.

than a disc of air. In Charts 3 and 4 the following characteristics are exhibited:—

- (i) The lines of direction converge on, or diverge from, the faces of the disc.
- (ii) Marked increases are produced in the displacement amplitude near either face.
- (iii) Marked diminution is produced in the pressure amplitude near either face.
- (iv) Regions of confused direction are produced in which the oscillations of the water particles are obviously no longer rectilinear. At some points the confusion amounts to a total loss of direction.
- (v) It was also observed that marked changes of quality are in general produced. Thus in the case of the oiled silk disc the quality of the sound observed near the face suggested that the higher frequencies were largely suppressed.

If the bounding wall of the disc consists of material having appreciable rigidity, such as tin-plate or lead, the surface appears to vibrate in sections producing very sharply marked and localised disturbances (*vide* Chart 5, *et seq.*). The variations of quality are particularly marked, sometimes the fundamental and sometimes the harmonics being emphasised. Not only may the quality change rapidly from point to point, but it may vary even at a given point as the displacement explorer is rotated. The impression is received that two distinct trains of waves of different frequencies are passing simultaneously through the point under observation.

The hollow disc may be regarded as in some sense the theoretical converse of the solid disc. Unless the walls are very thick, the hollow disc will be more compressible than water, and will therefore tend to act as a simple source, giving rise to secondary waves in *opposite* pressure phase to the primary waves. If, as in the case of the oiled silk and tin-plate discs, the mean density is less than that of water, the amplitude of the disc as a whole will exceed that of the water particles in the undisturbed field (unless constrained by the support); and the disc will tend to act as a double source, giving rise to secondary waves of opposite pressure phase at the front surface and of similar phase at the back surface.

An examination of the charts shows that the "simple source" effect entirely outweighs any "double source" effect which may be present. It will be observed also that the distribution of direction near the disc is determined predominantly by the secondary field.

The regions of confused direction would be the resultant of the primary and secondary waves, occurring where these waves cross one another with a phase difference other than  $0^\circ$  or  $180^\circ$ .

The sectional vibration exhibited in Charts 5 *et seq.* is presumably due to the tendency of the elastic bounding plate of the disc to break up into sections having a natural period corresponding with that of the primary sound, and the peculiar local emphasis of the primary components may be ascribed to a difference in the sectional response to the component frequencies.

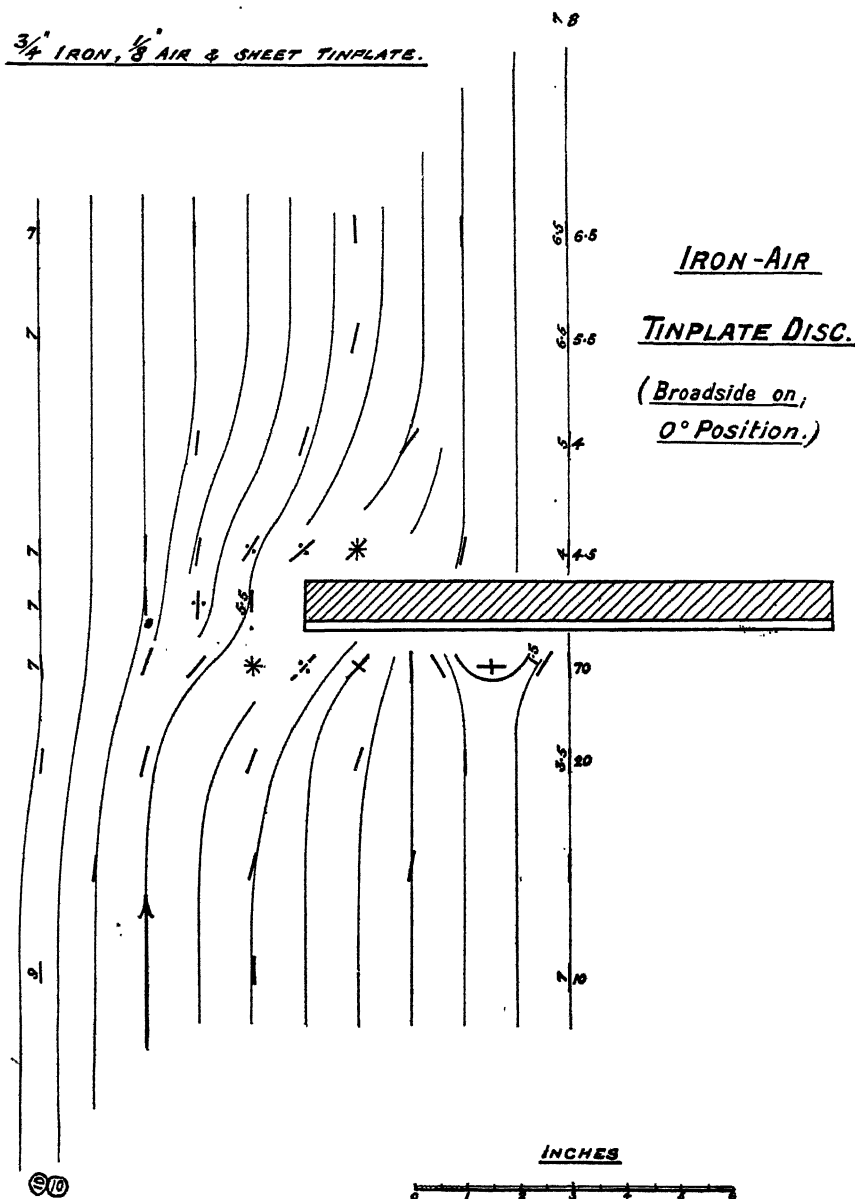


CHART 5.



(3) *Combinations of Types 1 and 2.*—As would be expected, various compromises between the characteristics of solid and hollow bodies may be produced by suitably constructed screens, though the more pronounced hollow body characteristics naturally tend to predominate.

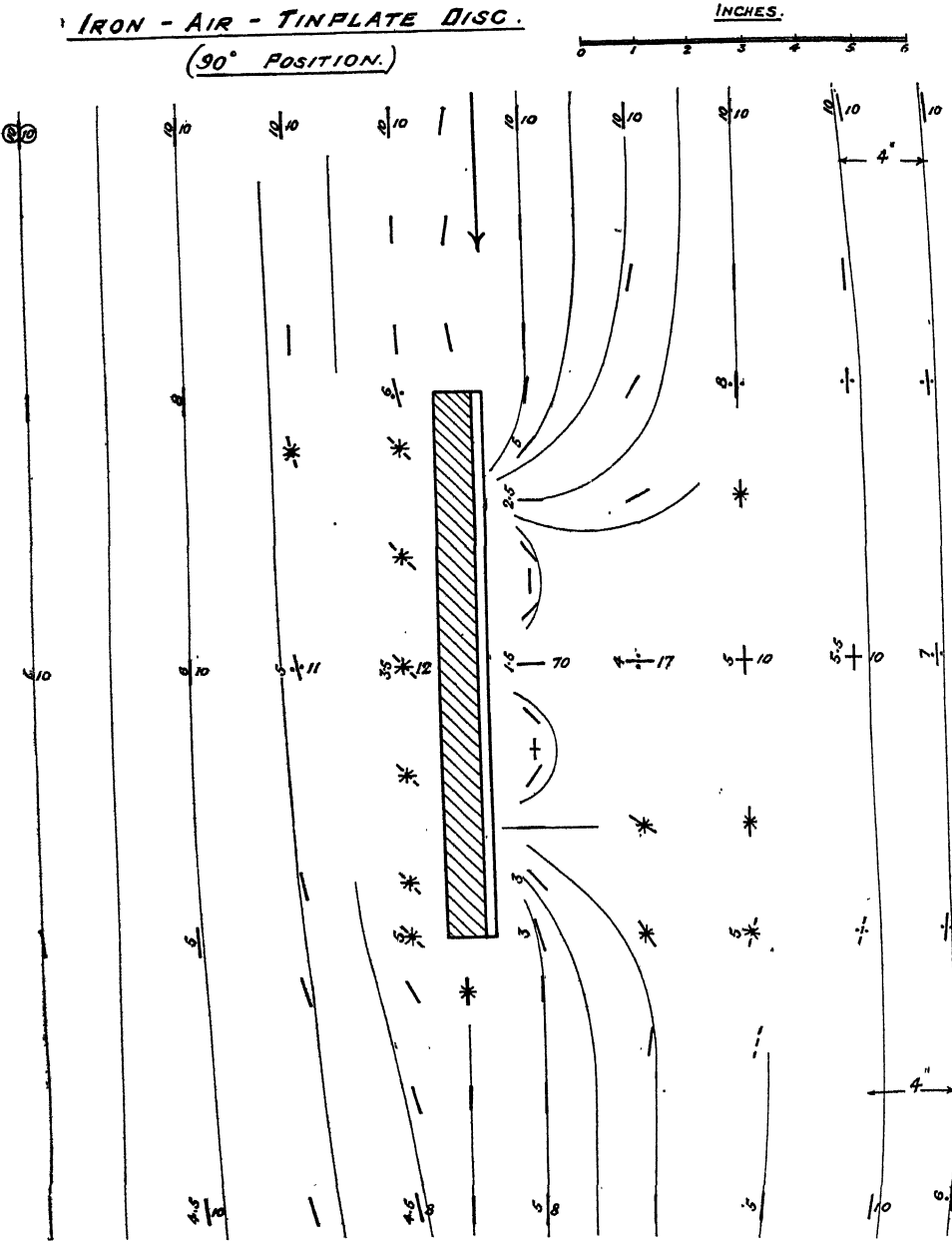


CHART 6.

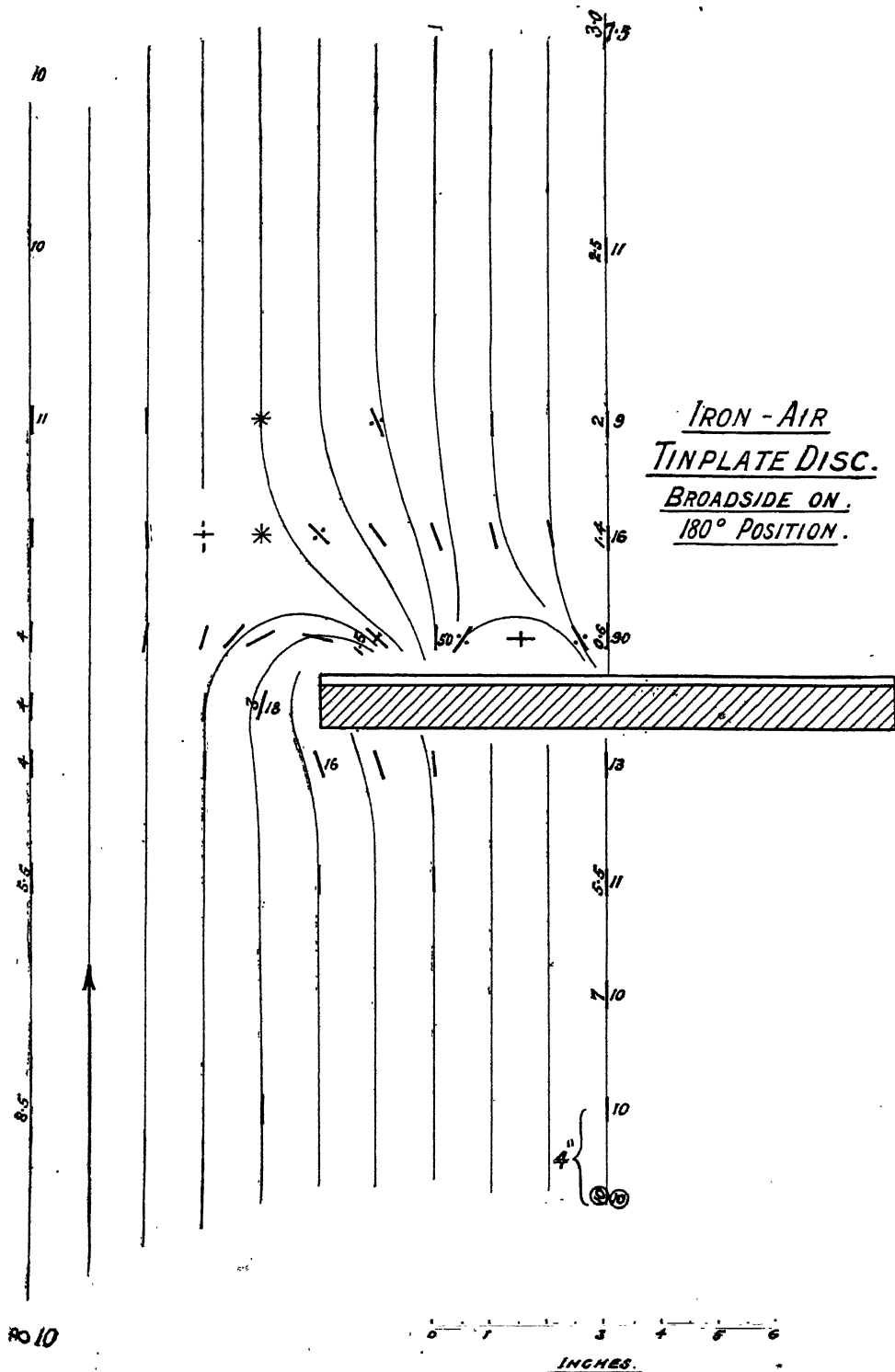


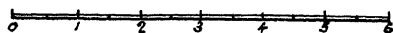
CHART 7.

(i) The Iron-air-tin-plate Disc (*vide* Charts 5, 6, 7) is an example of such a compromise. Details of construction are given on Chart 5. It may be noted that Chart 5 exhibits some semblance of a true shadow, the region behind the disc showing a simultaneous reduction of both kinetic and potential energy.

(ii) The Lead-wood Disc, which forms the baffle plate of the direction finder (*vide* Charts 10, 11, 12), shows very definite hollow body characteristics, which must be due to the presence of a film of air between the lead and the wood. These characteristics are modified, however, by the presence of the

### LEAD - PARAFFIN DISC.

INCHES.



217

240

210

\*

217



(A) CONTAINING AIR FILM.

29

28

210

|

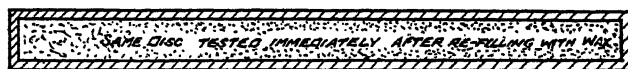
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217



(B) FREE FROM AIR.

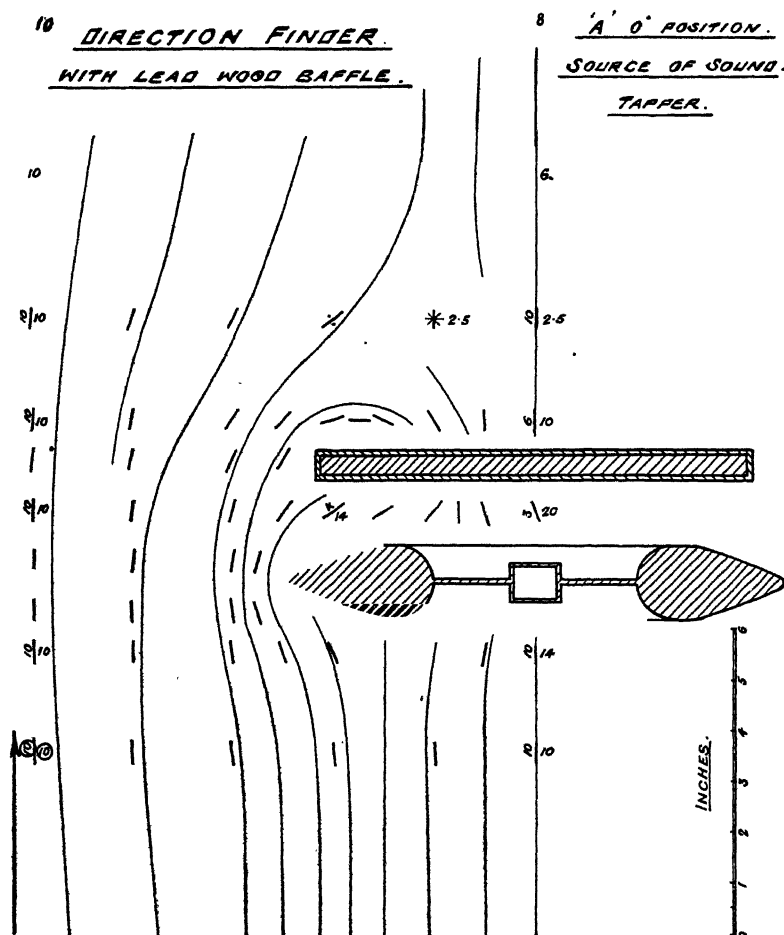


the pressure amplitude is shown at the back of the disc, of which no explanation can be offered.

The two charts illustrate the important effect produced by even a small trace of air.

(4) *Single Diaphragm Direction Finder.* (i) Direction Finder without Baffle (Chart 9).—This instrument is briefly described in Section 1. The field does not differ essentially from that which was obtained for a single metal ring (chart not shown). It appears as if the bronze diaphragm does not appreciably modify the sound distribution. As in the case of the lead disc, the pressure amplitude is sensibly uniform throughout the field.

(ii) Baffled Direction Finder (Charts 10, 11, 12).—Charts are shown for the instrument in the position of maximum, the position of minimum, and the



edge-on position. The exploration is confined to the immediate neighbourhood of the diaphragm and baffle.

DIRECTION FINDER WITH LEAD-WOOD:-

BAFFLE, "C", 30° POSITION.

SOURCE OF SOUND:- TAPPER.

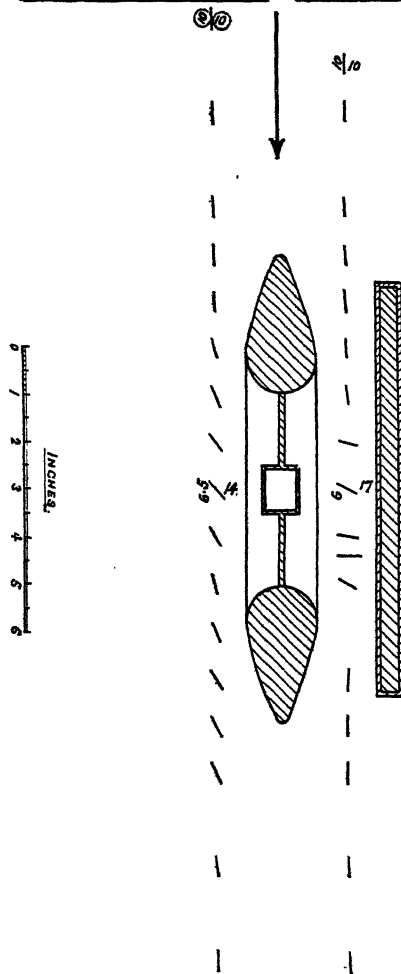


CHART 11.

The field of the baffle plate has already been commented upon. Further remarks are deferred to Section 4.

### *DIRECTION FINDER AND LEAD WOOD BAFFLE.*

**'B' 180° POSITION.**

SOURCE OF SOUND:- TAPPER.

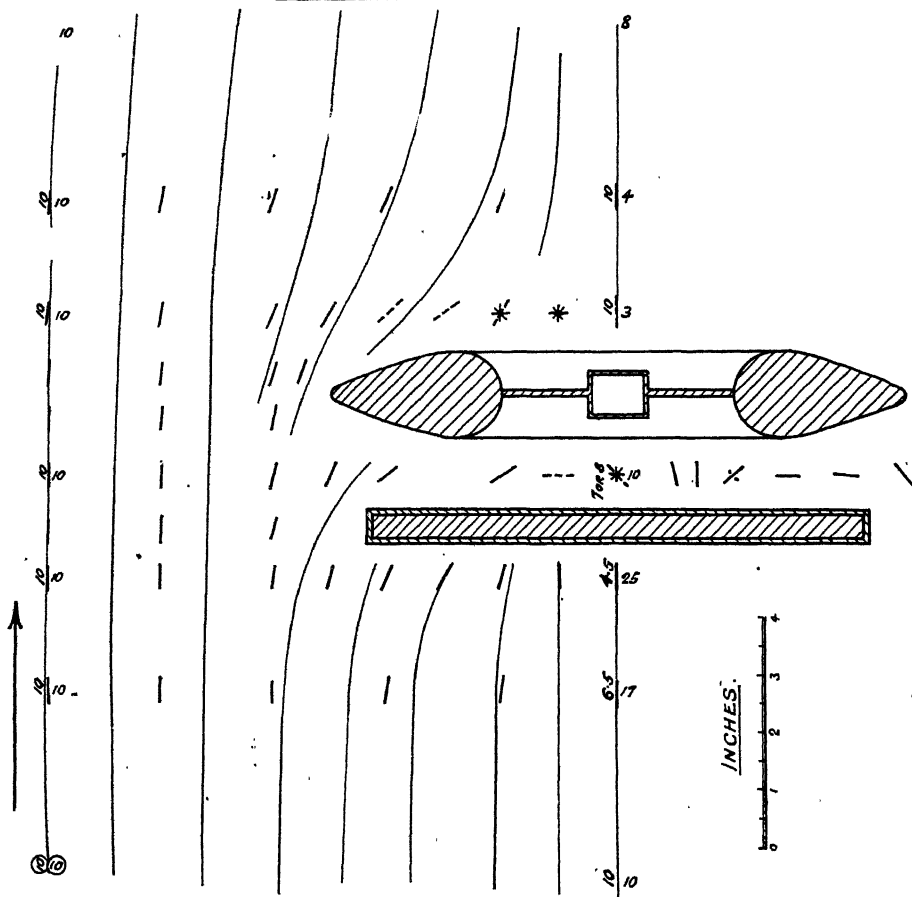


CHART 12.

### 3. EXPERIMENTS WITH BAFFLE PLATES.

As previously stated, solid discs of lead or other materials had been found to be practically ineffective as baffle plates, whilst the lead-wood discs gave the instrument a definite bias. Since the chart indicated that the most important difference between these discs lay in the air films enclosed in the composite disc, the conclusion was drawn that this air film plays an essential part in the baffle.

This conclusion was verified by a number of experiments with "air-film"

baffles consisting of two plates of metal pressed into contact and soldered around the edge. Many baffles thus constructed gave very good bias.

The various patterns of baffle, however, shared with the lead-wood baffle the defect of lack of reproducibility, baffles carefully made to the same specification giving results of very different quality. Hence the experiments are not described in detail. A short account is given, however, of the characteristics of a typical baffle plate, whilst some experiments with "stream-line" baffle plates are briefly described as demonstrating the striking influence of small traces of air.

*(a) Characteristics of a Typical Baffle Plate.*

The curves shown in fig. 5 represent the effect produced by a typical baffle plate and the variation of that effect with distance. The baffle employed consisted of two plates of sheet iron 10 inches in diameter and 1/20 inch thick, pressed together and soldered round the edge.

A series of "rotation curves" was made for various distances,  $d$ , of the baffle plate from the diaphragm by rotating the instrument through various angles from its position of maximum and measuring the change in the amplitude of response by the potentiometer shunt method. The distance,  $d$ , of the baffle from the diaphragm was successively diminished. Selected rotation curves are shown in fig. 5 (*a*), (*b*), (*c*), (*d*), and the complete series of observations is recorded in diagram (*e*).

Curve (*a*) shows that when  $d$  is great the response of the instrument passes through a minimum at  $\pm 90^\circ$ , whilst at  $180^\circ$  the response rises to a maximum equal to that at  $0^\circ$ .

As the baffle is brought in toward the diaphragm the maximum at  $180^\circ$  is reduced relatively to that at  $0^\circ$ , whilst the lateral minima at  $90^\circ$  become less marked and at the same time move toward the suppressed maximum (curve (*b*)).

The changes mentioned continue progressively until the lateral minima fade out, whilst the maximum at  $180^\circ$  is so far reduced as to become a minimum (curve (*c*)).

If the distance of the baffle is reduced below a certain value the minimum at  $180^\circ$  begins to fade out, and finally the direction finder loses its directional properties entirely, responding equally for all orientations (curve (*d*)).

Diagram (*e*) represents the progressive changes as the distance of the baffle is altered. The curve "amp.  $180^\circ$ " indicates the amplitude of response at  $180^\circ$  and the curve  $l/0$  the amplitude of response at the lateral minimum relatively to that at  $0^\circ$ .

In diagram (*e*) the amplitude of response at  $0^\circ$  has been taken as standard. By arranging the baffle so that it could quickly be swung into or out of



action at will, it was found that this amplitude is not constant but increases as  $d$  is reduced. The variation of amp.  $0^\circ$  with  $d$  is shown in diagram (f), which

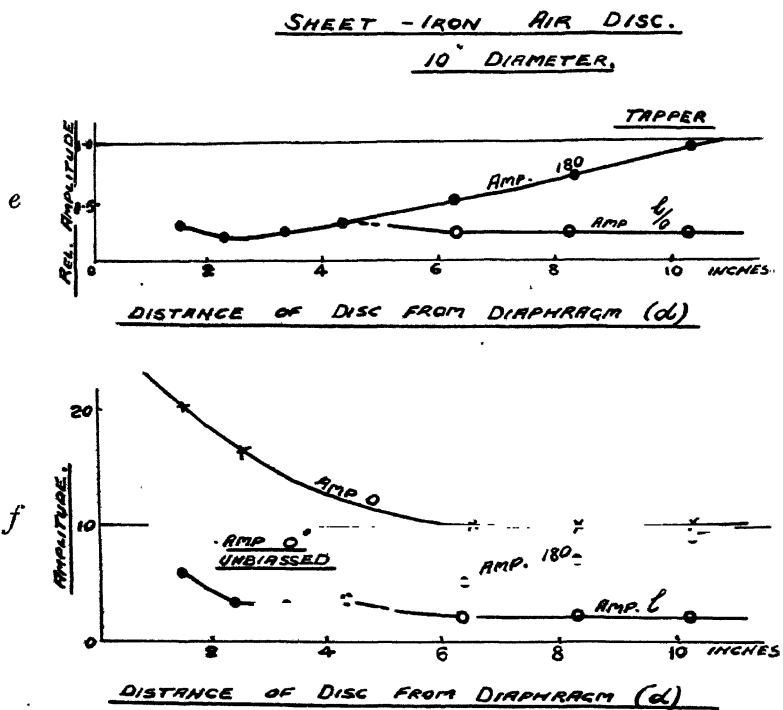
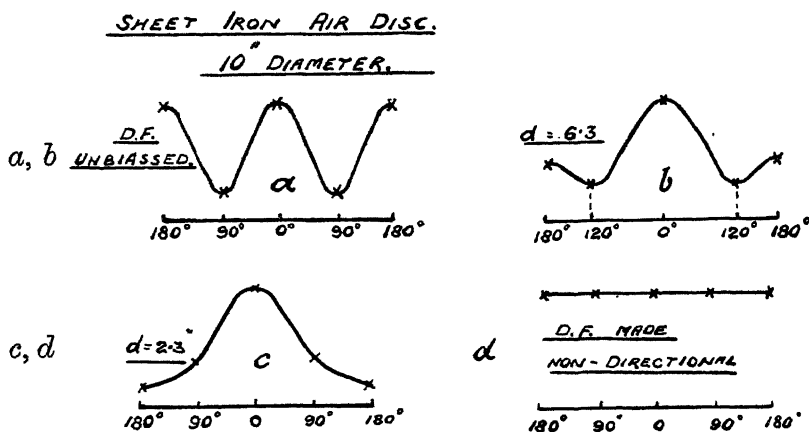


FIG. 5.

shows also the true variation of amplitude at  $180^\circ$  and at the lateral minima.

Though diagram (f) gives the fuller information, diagram (e) is of greater

practical significance, since the increase in sensitivity produced by the baffle is of less importance than its effect upon the ratio amp.  $180^\circ/0^\circ$ . From (e) it is seen that the correct setting for the baffle employed is at about 2.3 inches from the diaphragm. At this distance amp.  $180/0$  is about  $1/5$ .

The diagrams shown are representative of those obtained with good baffle plates. The chief practical consideration is that the curve amp.  $180/0$  shall have as low a minimum as possible; and this appeared to depend upon a critical adjustment of the air film. In the case of the lead-wood baffle (which was the earlier service form) the desired adjustment was secured largely by a process of selection.\*

The position and value of the minimum in the curve amp.  $180/0$  was found to vary not only from baffle to baffle, but also to a smaller extent in the same baffle with sounds of different quality and pitch.

(b) "Stream-line" Baffle Plates.

When a direction finder is employed in rough water or in a current, considerable noise is produced in the telephone receivers by the wash of the water. With a view to diminishing such disturbances wooden discs were secured flush with the ring of the instrument to enclose the diaphragm between them, small holes being left for the escape of the air. It was found that, though the directional properties of the instrument were not impaired, a marked bias was produced. The effect is recorded in fig. 6(a),

FIG. 6.

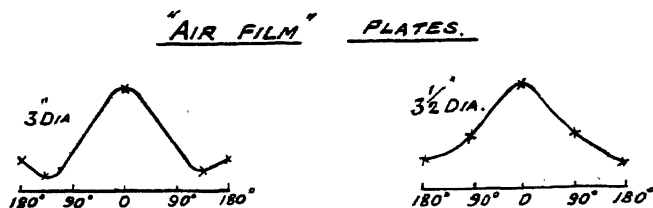
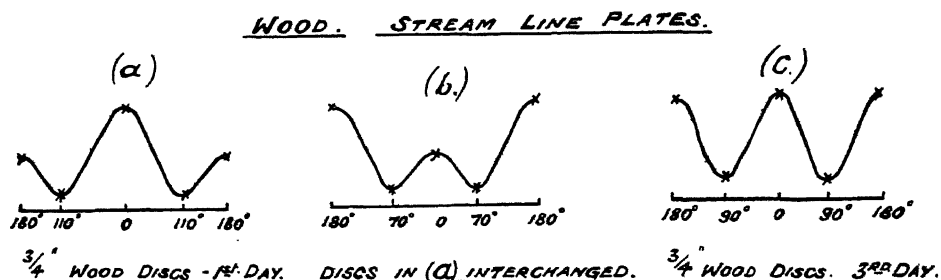


FIG. 7.

\* A more reproducible design of baffle was later produced by Dr F. L. Hopwood.

where the curve represents the change in the amplitude of the response as the instrument was rotated in either direction from one of its broad-side on positions. By interchanging the discs the direction of the bias was reversed (curve (b)). The strength of the bias diminished as the wooden discs became sodden, and after a day or two disappeared (curve (c)).

The bias was attributed to the presence of air in the pores of the wood, which was differently distributed in the two discs. Attempts were made to reproduce these discs in more permanent form. The wooden discs were replaced by discs of tin-plate, to the centre of one of which a smaller tin-plate disc was soldered by the edges only, so that an air film was enclosed. As shown in fig. 7, very good bias was obtained with selected air films, 3 to 3½ inches in diameter.

These experiments demonstrate the predominant importance of the air in a baffle plate, and the unimportance of the mass of the plate.

#### 4. NOTES ON THEORY OF SINGLE PLATE DIRECTION FINDER.

A complete theory of the unbiased direction finder would involve a consideration not only of the movements of the diaphragm but also of the ring. An approximate explanation, however, may be attempted by supposing that the heavy ring remains practically at rest whilst the diaphragm is driven to and fro by the resultant action of the pressure pulses arriving at the two faces, A and B. Let the pressure pulses arriving at these faces be respectively  $P_1 \cos 2\pi nt$  and  $P_2 \cos (2\pi nt - \alpha)$ ; then if  $Q$  is the amplitude of the resultant force acting on the diaphragm

$$Q = \sqrt{(P_1^2 + P_2^2 - 2P_1P_2 \cos \alpha)}.$$

In actual fact both pressure amplitude and phase may vary over each surface of the diaphragm, so that  $P_1$ ,  $P_2$ , and  $\alpha$  represent the effective values.

If the instrument is turned edge-on to the source, then, from considerations of symmetry,  $P_1 = P_2$  and  $\alpha = 0$ , whence  $Q = 0$  and the diaphragm fails to vibrate.

Let surface A be turned toward the source of sound and at right angles to the direction of propagation. From Chart 9 we learn that there is no appreciable difference of pressure amplitude between opposite faces of the diaphragm. Writing therefore  $P_1 = P_2 = P$ ,

$$Q = P\sqrt{(2 - 2 \cos \alpha)}.$$

We may regard the phase lag as due to the longer path travelled by the pulses reaching side B as compared with those falling on surface A.

The overall radius of the instrument is 5 inches, whilst that of the diaphragm is 2 inches. We may take 4 inches as the rough average distance of the

diaphragm from the edge of the clamping ring. If the frequency of the sound is 580 ~/sec., the wave-length is about 100 inches.

$$\text{Hence} \quad \alpha = \frac{2\pi \times 4}{100}, \text{ or about } 14^\circ,$$

$$\text{and} \quad Q = P \sqrt{(2 - 2 \cos 14^\circ)} = P \times 0.25 \text{ nearly.}$$

Now, if the water were excluded from side B, the amplitude of the force acting on the diaphragm would be  $P$ ; hence the ratio  $Q/P = 0.25$ . Tests made by Dr. F. L. Hopwood on the effect of thus excluding the water showed that the sensitivity is actually increased thereby from three to five times.

The action of the baffle plate is more obscure. The foregoing theory of the unbaffled instrument suggests that this plate, when interposed between the diaphragm and the source, may tend to bring the pressure pulses arriving at the surfaces A and B into phase by increasing the length of path to surface A. Such a theory would explain the suppression of the maximum at  $180^\circ$ , but fails to account for the observed reinforcement of the maximum at  $0^\circ$  or the obliteration of the minima at  $-90^\circ$ .

The general effects of the baffle plate might be explained on the assumption that the baffle introduces a constant phase lag near the adjacent face of the diaphragm, and that for the ideal unidirectional setting of the baffle this lag is equal to  $\alpha$ .

$$\begin{aligned} \text{Then} \quad & \text{in position} \quad 0^\circ, Q = P \sqrt{(2 - 2 \cos 2\alpha)}. \\ & \text{,,} \quad \pm 90^\circ, Q = P \sqrt{(2 - 2 \cos \alpha)}. \\ & \text{,,} \quad 180^\circ, Q = P \sqrt{(2 - 2 \cos 0^\circ)} = 0. \end{aligned}$$

Hence the maximum at  $0^\circ$  would be reinforced and that at  $180^\circ$  would be suppressed, whilst the minima at  $\pm 90^\circ$  would disappear.

Charts 10 to 12, however, indicate that, in addition to any modifications of phase, important modifications of pressure amplitude are also produced which are too great to be disregarded as incidental disturbances. It is possible that the symmetry produced by the baffle is a somewhat fortuitous resultant of the various disturbances which it introduces. Such a view receives support from the difficulty hitherto experienced in securing a baffle of good reproducible design, a considerable fraction of those made having to be rejected, owing to their failure, for no perceptible reason, to give good baffle action.

## APPENDIX.

*Exploration of the Acoustic Field produced in the Reservoir by a small Source of Sound.*

Though the large area of the reservoir rendered negligible the disturbances due to reflection from the banks, it was desirable to determine to what extent the primary acoustic field was affected by reflections from the surface and bottom.

For this purpose a dead calm day was chosen. By means of a graduated rope stretched from the raft to the shore, a boat was hauled to measured distances from the source of sound. A Submarine Signal Company's hydrophone, suspended on a graduated cable, was employed as a "pressure explorer."

(a) *Exploration with Buzzer (vide Section 2) as Source.*—The buzzer was supported in the water at a depth of 8 feet, as for the experiments of Section 2. As the hydrophone was lowered steadily to the bottom, it was observed that, in general, variations of intensity occurred, the sound received passing through a number of maxima and minima. The depth at which each minimum occurred was recorded. Special attention was paid to the first minimum below the surface zone, this being followed continuously from point to point as the boat was moved, so that the zone was completely traced. The results are plotted in fig. 8.

*Comments.*—(1) The zone AB, which was clearly marked, coincides approximately with the theoretical position of the interference zone, which is produced by reflection, with change of phase, from the surface.

(2) The zone BC, also clearly marked, is remarkable in its form, and cannot be accounted for by surface reflection only. This zone, together with the others (of which points only have been recorded), was probably produced as the result of multiple reflection from bottom and surface.

(3) Close to the bottom (which was in general of soft mud) there was usually observed some diminution of intensity. At some points, however, a reinforcement was observed, and in certain of such cases the instrument struck hard rock on reaching the bottom. The diminution may have been due to gases trapped in the mud, which would tend to produce reflection with change of phase.

(4) The intensity close to the surface was consistently very low, as would be expected from theory.

(5) The acoustic field seemed to tend toward uniformity as the distance from the source increased, the limits of the zones observed, from 66 feet to 160 feet, being increasingly indefinite.

(b) *Exploration with "Tapper" (vide Section 2) as Source.*—An attempt was made to carry out an exploration with the tapper as source in the same manner as with the buzzer. No definite maxima or minima were, however, observable, and only certain variations of quality could be distinguished. Regarding the tapper as a "noise source," this result would be anticipated.

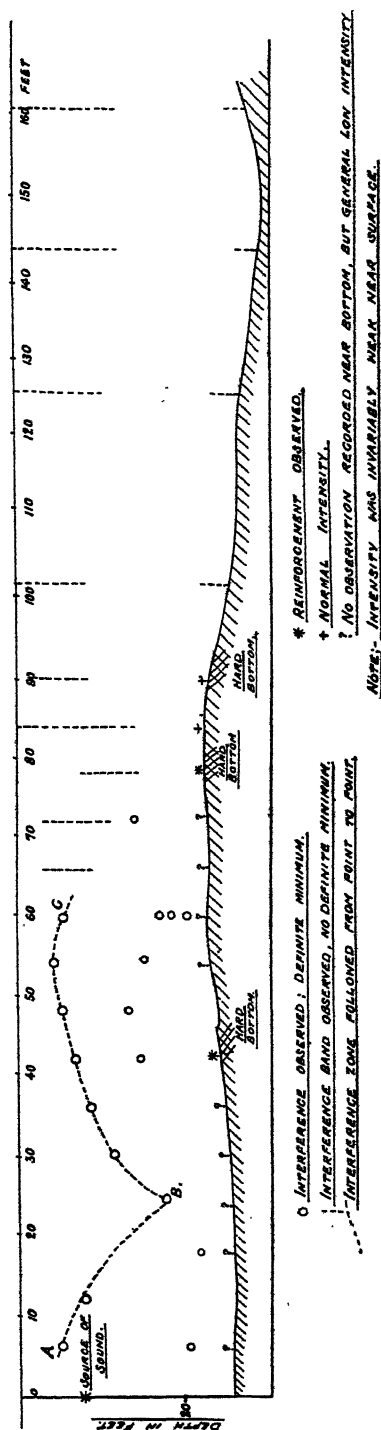
From the diagram it will be seen that, at the working distance of about 20 feet, and at the same depth as the buzzer, it would be unsafe to assume the "undisturbed" field to be uniform. That practical uniformity existed, however, may be inferred from the marginal readings of the majority of the charts, which indicate uniform distribution, except in cases in which the disturbance due to the disc under examination is obviously of wide extent.

#### SUMMARY.

The experiments described were undertaken primarily with the object of elucidating the action of the "single plate direction finder" and "baffle."

By means of a pair of miniature exploring hydrophones, the acoustic field was plotted around a number of discs placed in the path of plane waves propagated through the water of a reservoir, so large that reflections from the sides could be disregarded.

The characteristics displayed by the charts varied according as the discs were solid or contained air cavities. The *solid* bodies created comparatively



slight disturbances in the sound waves, no variations of pressure amplitude being perceptible. The *hollow* bodies created very pronounced disturbances of direction, amplitude of displacement, and pressure amplitude. Very small air cavities produced marked effects.

The lead-wood baffle plate of the direction finder showed pronounced hollow body characteristics, and, from experiments made with "stream-line" baffle plates containing slight air films, it was concluded that the air film between the lead and the wood constitutes the essential part of the baffle, the mass of the baffle plate being of minor importance.

The characteristics of a typical baffle plate were examined with special reference to the effect of varying the distance between diaphragm and baffle.

An approximate theory of the unbaffled instrument can be based on the existence of a phase difference between the pressure pulses arriving at the two faces of the diaphragm in the "broad-side on" position, this difference disappearing in the "edge-on" position.

No simple theory of the baffle plate can be offered which covers all the experimental facts.

In an appendix are given the results of an exploration of the distribution of sound in the reservoir due to a small submerged source. A source of definite frequency was found to produce marked interference zones, due apparently to multiple reflections from surface and bottom. A "noise" source produced no definite interference zones, though certain variations of intensity and quality were observed.

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*The Principles of Internal Ballistics.*

By J. PROUDMAN, University of Liverpool.

(Communicated by H. Lamb, F.R.S. Received June 11, 1921.)

1. This paper contains the results of an investigation carried out at the Research Department, Royal Arsenal, Woolwich. It is published by permission of the War Office. The principal features are the methods of determination of the rates of burning of propellants and the treatment of the mathematical equations relating to the motion of the shot in the gun. No attempt has been made to improve on the methods of treating the distribution of motion and pressure through the gases in the gun, the resistances to the motion of the shot, the conduction of heat through the metal of the gun, or the recoil of the gun.

The general theory is sketched in terms of functions which require experimental evaluation; and then assumed provisional forms are assigned to these functions.

The author wishes to state that he owes the foundation of his knowledge of the subject, and also the opportunity of making these investigations, to Messrs. F. B. Pidduck and A. D. Crow.

*General Theoretical Considerations.*

2. We shall assume that the density and pressure of the propellant gases determine the temperature, so that we have always an equation of the form

$$T = H(\Delta, P), \quad (1)$$

where  $\Delta$  denotes the density,  $P$  the pressure, and  $T$  the absolute temperature of the gases. We shall also assume that the chemical constitution of the gases is determined by the density and pressure, the attainment of chemical equilibrium being so rapid that the state appropriate to any pair of values of  $\Delta$  and  $P$  is reached before these values have been sensibly departed from. We can then treat the gases arising from the burning of a propellant as a single body, whose state is defined by  $\Delta$  and  $P$ , and all absorption or emission of heat due to changing chemical constitution may be allowed for in the specific heats taken.

Let  $E(\Delta, P)$

denote the intrinsic energy per unit mass of the gases when in the state given by  $\Delta$  and  $P$ . By intrinsic energy we mean the maximum amount of work which the gases can be made to do by allowing them to expand to zero



pressure and to cool to absolute zero of temperature. Let  $E$  denote the intrinsic energy per unit mass of the gases before they have done any work or lost any heat after being generated from the burning propellant. This we may call the intrinsic energy per unit mass of the unburnt propellant; it will depend only on the state of the unburnt propellant. The "uncooled pressure-density relation" will be

$$E(\Delta, P) = E. \quad (2)$$

If we plot  $P$  against  $\Delta$ , then the possible states of the gases will be given by all the points of an area, and (2) will be the equation of the upper boundary of this area.

Let  $\sigma_v$  and  $\sigma_p$  denote the specific heats at constant volume and constant pressure respectively; these will both be functions of  $\Delta$  and  $P$ . If we write

$$v = 1/\Delta, \quad (3)$$

so that  $v$  is the volume per unit mass of the gases, we have,  $J$  denoting the mechanical equivalent of heat,

$$\left. \begin{aligned} \frac{\partial}{\partial P} E\left(\frac{1}{v}, P\right) &= J\sigma_v \frac{\partial}{\partial P} H\left(\frac{1}{v}, P\right) \\ \frac{\partial}{\partial v} E\left(\frac{1}{v}, P\right) &= J\sigma_p \frac{\partial}{\partial v} H\left(\frac{1}{v}, P\right) - P \end{aligned} \right\} \quad (4)$$

A necessary consequence of these is

$$\frac{\partial}{\partial v} \left\{ J\sigma_v \frac{\partial}{\partial P} H\left(\frac{1}{v}, P\right) \right\} = \frac{\partial}{\partial P} \left\{ J\sigma_p \frac{\partial}{\partial v} H\left(\frac{1}{v}, P\right) - P \right\},$$

or

$$(\sigma_p - \sigma_v) \frac{\partial^2}{\partial v \partial P} H\left(\frac{1}{v}, P\right) + \frac{\partial \sigma_p}{\partial P} \frac{\partial}{\partial v} H\left(\frac{1}{v}, P\right) - \frac{\partial \sigma_v}{\partial v} \frac{\partial}{\partial P} H\left(\frac{1}{v}, P\right) = \frac{1}{J}. \quad (5)$$

Van der Waal's theoretical form for the function  $H(\Delta, P)$  is

$$RH(\Delta, P) = (P + a\Delta^2)(1/\Delta - b), \quad (6)$$

where  $R$ ,  $a$ ,  $b$ , are positive constants. If this law applied to the gases in question and if  $\sigma_v$  and  $\sigma_p$  were constants, we should have from (5)

$$\sigma_p - \sigma_v = R/J, \quad (7)$$

and then the integration of the equations (4) would give

$$(\gamma - 1) E(\Delta, P) = (P + \gamma a \Delta^2)(1/\Delta - b), \quad (8)$$

where  $\gamma = \sigma_p/\sigma_v$ .

The uncooled density-pressure relation (2) would become

$$(P + \gamma a \Delta^2)(1/\Delta - b) = E, \quad (9)$$

where

$$E = (\gamma - 1) E. \quad (10)$$

The equation (9) may be written in the form

$$\frac{P}{\Delta} = bP + \frac{\Pi}{1 + \gamma a \Delta^2 / P}, \quad (11)$$

so that if we plot  $P/\Delta$  against  $P$ , we obtain a curve which has for an asymptote

$$P/\Delta = bP + \Pi, \quad (12)$$

and always lies below this asymptote, except on the axis of  $P = 0$ , where the two meet. Equation (12) expresses Noble and Abel's pressure-density relation.

When a piece of homogeneous and isotropic propellant is surrounded by gas in a uniform state, we assume that combustion takes place by parallel layers. If  $u$  denotes the *rate of burning* down any normal, we shall suppose it determined by the state of the gases, so that

$$u = U(\Delta, P). \quad (13)$$

Let us consider an explosion in which all the constituent pieces of the charge are exactly alike, have been ignited all over their surfaces at exactly the same instant, and the state of the gases in contact with the unburnt charge is continuously uniform.

Let  $v_0$  denote the volume and  $s_0$  the total surface of a piece of propellant before ignition. At any time,  $t$ , during the explosion, let  $z$  denote the fraction of the charge burnt, and  $s$  the total surface of each piece. We shall have

$$s = s_0 \phi(z), \quad (14)$$

this defining  $\phi(z)$ , Charbonnier's form-function, and also

$$v_0 dz/dt = us, \quad (15)$$

which give

$$\frac{dz}{dt} = \frac{s_0}{v_0} u \phi(z). \quad (16)$$

In ballistic applications we require the functions

$$E - E(\Delta, P), \quad U(\Delta, P),$$

for all the values of  $\Delta$  and  $P$  that occur. The function  $H(\Delta, P)$  and the specific heats  $\sigma_v$  and  $\sigma_p$  may occur as auxiliaries in ballistic investigations, but, on the present assumptions, need not enter explicitly into practical ballistic calculations.

### *Closed Vessel Explosions.*

3. Let us first consider an ideal closed vessel with non-conducting walls, and let us suppose that the attainment of mechanical equilibrium is so rapid that  $\Delta$  and  $P$  may be taken as uniform through the vessel at any stage of the explosion.

Let  $\Delta_1$  and  $P_1$  denote the maximum final values of  $\Delta$  and  $P$  respectively. The relation between  $\Delta$  and  $P$  will, throughout the explosion, be given by (2) and may be found from that between  $\Delta_1$  and  $P_1$  in different explosions. If  $\delta$  denote the density of the unburnt propellant, supposed uniform and constant throughout the explosion, we have

$$z = \frac{1/\Delta_1 - 1/\delta}{1/\Delta - 1/\delta}, \quad (17)$$

it being supposed that there is no non-gaseous residue after the explosion.

We suppose that the record gives  $P$  as a function of  $t$ ; then (2) gives  $\Delta$  and (17)  $z$  as functions of  $t$ . Using (16), we obtain  $u$  as a function of  $t$ ,  $z$ ,  $\Delta$  or  $P$ . It is to be noted, however, that we have only considered here the determination of the function  $U(\Delta, P)$  for the gases in the uncooled state; that is, only for the upper boundary of the representative area in the  $\Delta, P$  plane over which the function is required.

If, after the explosion, we could draw off the heat from the gases so as to keep  $\Delta_1$  constant and  $\Delta$  and  $P$  uniform through the vessel, and could take a record of the quantity of heat,  $Q$ , given off, as a function of  $P$ , we should have

$$JQ = E - E(\Delta_1, P), \quad (18)$$

so that  $E - E(\Delta, P)$  could be determined for all desired states.

Now let us suppose that the release-valve of the vessel is connected with that of another vessel whose walls are conducting. Let both vessels be charged and the valve kept closed until the charge in the conducting vessel has been exploded and the gases allowed to cool. Now let the valve be opened, so that some of the cooled gases pass into the non-conducting vessel and reach a density  $\Delta_0$  and pressure  $P_0$  round the unburnt charge of density  $\Delta_1$ . Next let the valve be closed and the charge fired, and suppose it burns sufficiently slowly for all the gases in the vessel to be continuously in a uniform state. If this state be given by  $\Delta, P$ , we shall have

$$z = \left(1 - \frac{\Delta_0}{\Delta}\right) \frac{1/\Delta_1 - 1/\delta}{1/\Delta - 1/\delta}, \quad (19)$$

$$\left(\frac{1}{\Delta} - \frac{1}{\delta}\right) \{E(\Delta, P) - E(\Delta_0, P_0)\} = \left(\frac{1}{\Delta_0} - \frac{1}{\Delta}\right) \{E - E(\Delta, P)\}. \quad (20)$$

When the function  $E - E(\Delta, P)$  is known for all the values of  $\Delta$  and  $P$  in question, the equation (20) gives the relation between  $\Delta$  and  $P$  during the second explosion, the gases being now in a partially cooled state. The record for this second explosion is supposed to give  $P$  as a function of  $t$ ; by means of (20) we obtain  $\Delta$  as a function of  $t$ , and by means of (19)  $z$  as a function of  $t$ . On again using (16) we can then calculate the rate of burning,  $u$ , for

states other than uncooled ones. A means is thus indicated for the determination of the function  $U(\Delta, P)$  for all values of  $\Delta$  and  $P$  required.

If we assume

$$E(\Delta, P) = \frac{1}{\gamma-1} P \left( \frac{1}{\Delta} - \frac{1}{\delta} \right), \quad (21)$$

which is obtained from (8) by the usual practice of taking  $a = 0$ ,  $b = 1/\delta$ , we obtain from (20)

$$P - P_0 = \frac{\Pi(1/\Delta_0 - 1/\Delta)}{(1/\Delta_0 - 1/\delta)(1/\Delta - 1/\delta)}, \quad (22)$$

as the relation between  $\Delta$  and  $P$  during the second explosion.

### Cooling.

4. So far we have imagined ideal conditions. When we come to consider explosions in actual vessels, the loss of heat by conduction through the walls is a serious factor. It is obvious that with the same density of loading in the same vessel the maximum pressure will decrease as the duration of the explosion increases, and the effect has been noticed ever since accurate experiments were made. It is also clear that for those shapes of pieces of propellant which make

$$\phi(z) \rightarrow 0, \quad \text{as } z \rightarrow 1,$$

there will, at the instant of maximum pressure, be a certain fraction of the charge unburnt. For maximum pressure occurs when the rate of gain in pressure due to burning is balanced by the rate of loss in pressure due to cooling, and for the shapes in question the rate of gain by burning vanishes with the fraction of the charge unburnt. Further, for the same rate of loss by cooling, the fraction unburnt at maximum pressure will be greater the greater the duration of the explosion, or, practically, the greater the size of the piece of charge. The fall in maximum pressure from one explosion to another with the same density of loading, but with a larger size of piece of propellant, is therefore in excess of that representing a loss of energy through the walls of the vessel.

There exists, however, an important cooling phenomenon of a different type. This appears to have been first noticed by R. Blochmann\* for high explosives. He found that for the same density of loading the pressure increased as the value of  $S/C$  decreased,  $S$  denoting the total internal surface of the explosion vessel and  $C$  its capacity, and he determined the limiting value of the pressure as  $S/C \rightarrow 0$ .

For propellants, the diminution of maximum pressure due to cooling had

\* 'Dingler's Polytechnisches Journal, vol. 318, p. 234 (1903); the author owes this and many other references to Mr. F. B. Pidduck.

been elucidated in the Department. As was to be expected, it had been found that, for the same vessel and value of  $\Delta_1$ , the value of  $P_1$  increased as the duration of the explosion decreased. For each value of  $S/C$  and  $\Delta_1$  taken, the limiting value of  $P_1$ , as the duration tended to zero, was estimated. It was then found that, for the same value of  $\Delta_1$ , these limiting values of  $P_1$  increased as the values of  $S/C$  decreased, this being of the same nature as Blochmann's result. For each value of  $\Delta_1$  taken, second limiting values of  $P_1$  as  $S/C \rightarrow 0$  were found. These second limiting values of  $P_1$  were taken to represent the results of an ideal explosion in which no cooling takes place, and from them the uncooled pressure-density relation (2) was constructed. Further experiments of the kind are urgently required, great attention being paid to the temperature conditions of the vessel and propellant, and to the regularity of size and shape in the pieces of propellant.

*Apparent Rates of Burning.*

5. During an actual explosion, we do not know the true relation between  $\Delta$  and  $P$ , and so  $z$  cannot be found accurately as a function of  $t$  for the purpose of calculating the rate of burning by (16).

The method indicated at the beginning of § 3, when applied as if no cooling took place, is practically that established by Vieille,\* and hitherto, in no available publication on rates of burning, have cooling effects been eliminated or allowed for. Previous to Vieille's work, writers on ballistics had usually taken

$$u = u'P^\alpha, \quad (23)$$

$u'$  and  $\alpha$  being constants. For  $\alpha$  different writers had used

$$0, \frac{1}{4}, \frac{1}{2}, \frac{2}{3}, \frac{3}{4}, 1.$$

Vieille decided on the same law, as an approximation, for the propellants with which he experimented, and took for  $\alpha$

$$\frac{2}{3}, \frac{5}{9}, \frac{3}{4},$$

for nitrocellulose, cordite, and ballistite respectively.

For all the French propellants, Charbonnier, Gossot and Liouville claim the validity of (23), but whereas Charbonnier† maintains that  $\alpha = 1$ , Gossot and Liouville‡ insist that  $\alpha = \frac{2}{3}$ . For cordite M.D., heated to 80° F. before ignition, Mansell§ found the relation

$$u = u_0 + u_1 P, \quad (24)$$

$u_0$  and  $u_1$  being constants.

\* 'Mémorial des Poudres et Salpêtres,' vol. 6 (1893).

† See, e.g., 'Balistique Intérieure,' p. 76 (Paris, 1908).

‡ See 'Mémorial des Poudres et Salpêtres,' vol. 13 (1906).

§ 'Phil. Trans., A, vol. 207, pp. 243-262 (1907).

Both (23) and (24) make  $u$  independent of  $\Delta$ , and it is impossible to obtain  $u$  as a function of more than one independent variable by the methods that have been used. By these methods, each record leads to a relation between  $u$  and  $P$ , which, when the duration of the explosion is not too long, is an approximation to the true relation with  $\Delta$  connected to  $P$  according to (2).

It is clear, however, that as for the same value of  $P$  in different explosions we may have different values of  $\Delta$ , we may expect the derived relation between  $u$  and  $P$  to vary from the analysis of one record to that of another. On the one hand, the relation between  $\Delta$  and  $P$  cannot always be that assumed in the analysis, and, on the other hand, the true rate of burning may vary with the value of  $\Delta$  for the same value of  $P$ .

A first step in the study of true rates of burning is the elimination of cooling effects during the whole of the explosion. This requires an elaborate series of experiments, such as those already referred to. When the customary methods are used, we refer to the results as "apparent."

An apparent rate of burning is stated as a function of the pressure only; this function varies with the circumstances of the explosion, such as the size and shape of the vessel, the size of the pieces of propellant, the density of the charge, the temperature of the vessel and of the charge.

### *Uncooled Rate of Burning.*

6. We shall now show how to apply to the whole of the pressure-time records a double limiting process, so as to eliminate cooling effects.

We still make all the assumptions stated at the beginning of § 3, except that relating to cooling. From each record we calculate  $\dot{y}v_0/s_0$  as a fraction of  $y = P/P_1$ . In the absence of cooling effects, this relation would depend only on  $\Delta_1$  and be independent of  $v_0/s_0$  and  $S/C$ . On this account, and also because it obviates the uncertainty of corresponding times in different explosions, it is this relation between  $\dot{y}v_0/s_0$  and  $y$ , and not that between  $P$  and  $t$ , which is subjected to the limiting process.

We suppose that we have pressure-time records for each of  $m$  values of  $v_0/s_0$  in closed vessels having  $n$  values of  $S/C$ . For each value of  $S/C$ , and each of the values

$$0.1, 0.2, 0.3, \dots 0.9, 1,$$

of  $y$ ,  $\dot{y}v_0/s_0$  is plotted against the values of  $v_0/s_0$ .

From each set of  $m$  points thus obtained, the limiting value of  $\dot{y}v_0/s_0$  as  $v_0/s_0 \rightarrow 0$  is estimated. We are thus enabled to plot the limiting relation between  $\dot{y}v_0/s_0$  and  $y$  for each value of  $S/C$ .

Again for each of the values

$$0.1, 0.2, 0.3, \dots 0.9, 1$$

of  $y$ , the limiting values of  $\dot{y}v_0/s_0$  already found are plotted against the corresponding values of  $S/C$ . From each of the set of  $n$  points thus obtained, the second limiting value of  $\dot{y}v_0/s_0$  as  $S/C \rightarrow 0$  is estimated.

We are thus able to plot the double limiting relation between  $\dot{y}v_0/s_0$  and  $y$ , and this is taken as corresponding to an explosion in which there are no cooling effects. We now suppose that our symbols refer to this hypothetical explosion, and use the method sketched at the beginning of § 3.

From (17)  $z$  can be calculated as a function of  $y$ , since  $\Delta$  is connected with  $P$  by the "uncooled" relation. From (16) we have

$$u = \dot{y} \frac{v_0}{s_0} \frac{1}{\phi(z)} \frac{dz}{dy}, \quad (25)$$

from which  $u$  can be calculated as a function of  $y$ , and therefore of  $P$ . This represents the "uncooled" rate of burning function, *i.e.*, the function (13), when  $\Delta$  and  $P$  are connected by (2).

#### *Vessel of Variable Capacity.\**

7. Let unit charge be placed in a vessel with non-conducting walls whose capacity is variable, and let  $z$  denote the fraction burnt when the capacity is  $v$ . Then we have

$$\Delta = \frac{z}{v - (1-z)/\delta},$$

still regarding  $\delta$  as uniform and constant.

The total intrinsic energy in the vessel is

$$(1-z)E + zE(\Delta, P),$$

and we deduce

$$\frac{d}{dv} z \{E(\Delta, P) - E\} + P = 0. \quad (26)$$

This is the fundamental differential equation for the circumstances we are now considering, and if  $v$  be interpreted as the capacity of the vessel per unit mass of the charge, it is of general application. It is an equation between  $v$ ,  $z$  and  $P$  which cannot be integrated without further relation between these variables.

The non-integrability of the equation (26) may be seen from the consideration that the change in the state of the gases for given changes in capacity and amount burnt, must depend on the way these changes have been made, and not simply on the extent of the changes. If an expansion takes place

\* Cf. A. G. Hadcock, 'Roy. Soc. Proc.,' A, vol. 94, pp. 484-488 (1917).

with a small fraction burnt, a small amount of work is done by the low pressure; if the same expansion takes place with a large fraction burnt, a large amount of work is done by the high pressure. In these two instances the final intrinsic energies of the gases must be different, though the capacities and fractions burnt be the same.

In the absence of experimental knowledge of the function  $E(\Delta, P)$  we are again forced on the provisional assumptions. Assuming the formula (21) we have

$$z E(\Delta, P) = \frac{1}{\gamma-1} P \left( v - \frac{1}{\delta} \right), \quad (27)$$

since 
$$\frac{1}{\Delta} - \frac{1}{\delta} = \frac{1}{z} \left( v - \frac{1-z}{\delta} \right) - \frac{1}{\delta} = \frac{1}{z} \left( v - \frac{1}{\delta} \right). \quad (28)$$

On using (10) the equation (26) becomes

$$\frac{1}{\gamma-1} \frac{d}{dv} \left\{ P \left( v - \frac{1}{\delta} \right) - z \Pi \right\} + P = 0, \quad (29)$$

or 
$$\Pi \frac{dz}{dv} = \left( v - \frac{1}{\delta} \right) \frac{dP}{dv} + \gamma P. \quad (30)$$

### Equations of the Gun.

8. Let  $C$  now denote the capacity of the chamber of the gun,  $A$  the area of bore, and  $x$  the travel up to time  $t$ ; let  $m$  denote the effective mass of the shot,  $c$  that of the charge, and  $z$  the fraction burnt up to time,  $t$ ; also, let  $V$  denote the velocity of the shot and  $P$  the pressure of the gases at the time  $t$ . Then we have

$$v = (C + Ax)/c, \quad (31)$$

$$V = dx/dt, \quad (32)$$

and 
$$m dV/dt = (1-\beta) A (P-R), \quad (33)$$

where  $R$  and  $\beta$  are inserted to allow for resistance and the angular acceleration of the shot. The equation (26) yields

$$\frac{c}{A} \frac{d}{dx} z \{ E(\Delta, P) - kE \} + P = 0, \quad (34)$$

where 
$$\Delta = \frac{z}{(C + Ax)/c - (1-z)/\delta} \quad (35)$$

and  $k$  is inserted to allow for loss of heat through the walls of the gun.

The equations (32), (33), (34) and (16), we shall refer to as the "equations of the gun." Equations (33) and (34) give

$$m \frac{d}{dx} \left( \frac{1}{2} V^2 \right) + (1-\beta) c \frac{d}{dx} z \{ E(\Delta, P) - kE \} + (1-\beta) AR = 0, \quad (36)$$



which, on treating  $\beta$  as a constant, yields

$$\frac{1}{2} \frac{m}{1-\beta} V^2 + c\alpha \{E(\Delta, P) - kE\} + A \int_0^x R dx = 0, \quad (37)$$

using the conditions that when  $x = 0$ ,  $V = 0$ , and  $E(\Delta, P) = kE$ .

The equation (37) is the *energy integral*, and may be used instead of (33) and (34) in the equations of the gun.

We now again fall back on the provisional assumptions, and use the equation (30) and the law (24) for the rate of burning function. Equations (34) and (16) may therefore be written, on treating  $k$  as constant,

$$kc\Pi \frac{dz}{dx} = \left(C + Ax - \frac{c}{\delta}\right) \frac{dP}{dx} + \gamma AP, \quad (38)$$

$$\frac{dz}{dt} = (u_0 + u_1 P) \frac{s_0}{v_0} \phi(z), \quad (39)$$

the initial conditions being that motion begins at  $x = 0$  when  $P = R_0$ , the value of  $R$  at  $x = 0$ . Up to this stage we have

$$k\Pi z = (C/c - 1/\delta) P. \quad (40)$$

When *maximum pressure* occurs during burning, we have from (38)

$$kc\Pi dz/dx = \gamma AP,$$

and therefore, from (32) and (39)

$$\frac{V'}{\phi(z')} = \frac{kc\Pi}{\gamma A} \frac{s_0}{v_0} (u_1 + u_0/P'), \quad (41)$$

on using accents to denote evaluations under the circumstances of maximum pressure.

#### *Dimensional Relations.*

9. Take

$$\theta = 1 + \frac{Ax}{C - c/\delta}, \quad (42) \quad P = \frac{kc\Pi}{C - c/\delta} \cdot p, \quad (45)$$

$$M = \frac{(1-\beta)A^2v_0^2}{kc\Pi mu_1^2s_0^2}, \quad (43) \quad R = \frac{kc\Pi}{C - c/\delta} \cdot r, \quad (46)$$

$$V = (1-\beta) \frac{Av_0}{mu_1s_0} \cdot v, \quad (44) \quad \varpi = \frac{C - c/\delta}{kc\Pi} \cdot \frac{u_0}{u_1}, \quad (47)$$

and for the time instead of  $t$  take

$$\frac{v_0}{k\Pi u_1s_0} \left( \frac{C}{c} - \frac{1}{\delta} \right) \cdot t. \quad (48)$$

Then the equations of the gun may be written

$$d\theta/dt = Mv, \quad (49) \quad dz/d\theta = \theta dp/d\theta + \gamma p, \quad (51)$$

$$dv/dt = p - r, \quad (50) \quad dz/dt = (p + \varpi) \phi(z), \quad (52)$$

the initial conditions being that

$$\theta = 1, \quad v = 0, \quad p = z = r_0, \quad (53)$$

while the *energy integral* becomes

$$\frac{1}{\gamma-1}(z-p\theta) = \frac{1}{2} Mv^2 + \int_1^\theta r d\theta, \quad (54)$$

and the condition for *maximum pressure* when it occurs during burning

$$\phi'(z') = \frac{1}{\gamma M} (1 + \varpi/p'). \quad (55)$$

The solution of the equations of the gun is then seen to depend on the constants  $M$  and  $\varpi$ , and on the functions  $\phi(z)$  and  $r$ . These may remain the same over a considerable variety of circumstances from the point of view of applications, so that a gun calculation for one set of circumstances may be made to yield the solution for certain other sets of circumstances. This principle provides the proof of the *general theorem* immediately following.

If  $A, C - c/\delta, x, m, c, v_0/s_0, k\Pi, u_1, v_0, 1 - \beta,$

be multiplied by a parameter raised respectively to the powers

$$(A), (C), (x), (m), (c), (v_0), (\Pi), (u_1), (u_0), (\beta),$$

then  $V$  will be multiplied by the parameter raised to the power

$$(A) + (v_0) + (\beta) - (m) - (u_1),$$

$P$  will be multiplied by the parameter raised to the power

$$(c) + (\Pi) - (C),$$

*time* will be multiplied by the parameter raised to the power

$$(v_0) + (C) - (u_1) - (\Pi) - (c),$$

providing

$$(A) + (x) = (C),$$

$$(c) + (m) + 2(u_1) + (\Pi) = 2(A) + 2(v_0) + (\beta)$$

$$(\Pi) + (c) + (u_1) = (C) + (u_0),$$

and  $R$  be changed like  $P$ .

Certain special cases of this theorem have long been used; thus take

$$(A) = 2, \quad (C) = 3, \quad (x) = 1, \quad (m) = 3, \quad (c) = 3, \quad (v_0) = 1,$$

$$(\Pi) = (u_1) = (u_0) = (\beta) = 0,$$

and we have the theorem that similar guns similarly charged with the same propellant produce equal pressures and equal velocities in linearly similar times.

*General Differential Equation.*

10. The equations (49), (50), and (52) give

$$v = \frac{1}{M} \frac{d\theta}{dt}, \quad (56)$$

$$p = r + \frac{1}{M} \frac{d^2\theta}{dt^2}, \quad (57)$$

$$p + \varpi = \frac{d}{dt} \int_{r_0}^z \frac{dz}{\phi(z)}, \quad (58)$$

and then on taking  $r$  constant during band engraving, we obtain

$$\int_{r_0}^z \frac{dz}{\phi(z)} = \frac{1}{M} \frac{d\theta}{dt} + (\varpi + r_0)t. \quad (59)$$

On solving this equation for  $z$  we have, say,

$$z = Z \left\{ r_0, \frac{1}{M} \frac{d\theta}{dt} + (\varpi + r_0)t \right\}, \quad (60)$$

where the function  $Z$  depends on the function  $\phi(z)$ . Substituting in (54) we obtain, on rearrangement,

$$\theta \frac{d^2\theta}{dt^2} + \frac{1}{2}(\gamma-1) \left( \frac{d\theta}{dt} \right)^2 - MZ \left\{ r_0, \frac{1}{M} \frac{d\theta}{dt} + (\varpi + r_0)t \right\} + \gamma M r_0 \theta = (\gamma-1) M r_0, \quad (61)$$

which is a differential equation for  $\theta$  in terms of  $t$ .

For pieces of propellant with a constant burning surface, so that  $\phi(z) = 1$ , we have

$$Z \left\{ r_0, \frac{1}{M} \frac{d\theta}{dt} + (\varpi + r_0)t \right\} = r_0 + \frac{1}{M} \frac{d\theta}{dt} + (\varpi + r_0)t, \quad (62)$$

and the differential equation (61) becomes

$$\theta \frac{d^2\theta}{dt^2} + \frac{1}{2}(\gamma-1) \left( \frac{d\theta}{dt} \right)^2 - \frac{d\theta}{dt} + \gamma M r_0 (\theta - 1) = M (\varpi + r_0)t. \quad (63)$$

After band engraving, we take  $r = 0$  and obtain

$$\int_{z_1}^z \frac{dz}{\phi(z)} = \frac{1}{M} \frac{d\theta}{dt} + \varpi t - (v_1 + \varpi t_1), \quad (64)$$

where the suffix 1 refers to the end of band engraving. This gives

$$z = Z \left\{ z_1, \frac{1}{M} \frac{d\theta}{dt} + \varpi t - (v_1 + \varpi t_1) \right\}, \quad (65)$$

and on substituting in (54) we obtain, on rearrangement,

$$\begin{aligned} \theta \frac{d^2\theta}{dt^2} + \frac{1}{2}(\gamma-1) \left( \frac{d\theta}{dt} \right)^2 - MZ \left\{ z_1, \frac{1}{M} \frac{d\theta}{dt} + \varpi t - (v_1 + \varpi t_1) \right\} \\ + (\gamma-1) M r_0 (\theta - 1) = 0. \end{aligned} \quad (66)$$

Again, for pieces of propellant with a *constant burning surface*, this differential equation becomes

$$\theta \frac{d^2\theta}{dt^2} + \frac{1}{2}(\gamma-1) \left( \frac{d\theta}{dt} \right)^2 - \frac{d\theta}{dt} = M\varpi t + M \{z_1 - (v_1 + \varpi t_1) - (\gamma-1)r_0(\theta_1-1)\}. \quad (67)$$

When  $\varpi = 0$  so that the rate of burning of the propellant is proportional to the pressure, the method of the present section is not the most direct, and when  $\varpi \neq 0$  so that the rate of burning is not proportional to the pressure, the differential equations we have obtained cannot be integrated in terms of elementary functions. Of course, in any particular case we may obtain a numerical solution to any required degree of accuracy, by the methods of step-by-step integration, and in this way tables could be constructed giving the solution in terms of  $M$ ,  $\varpi$  and  $r_0$  for each form of  $\phi(z)$ . But the transformations of the present section make a contribution to the results of the next section.

#### *Concentrated Band, Characteristic Parameters.*

11. By concentrated driving band we mean the conditions presented by

$$r = 0, \quad \text{for } \theta > 1; \quad r_0 \neq 0,$$

which is Charbonnier's method of treating band engraving.

The solution of the equations of the gun is then determined completely by the function  $\phi(z)$  and the values of

$$M, \quad \varpi, \quad r_0, \quad \theta_3, \quad (68)$$

the suffix 3 referring to the muzzle. In particular, the value of  $v_3$  and whether the charge is all burnt or not, depend only on these. If the charge is all burnt in the gun, then whether the maximum pressure occurs while it is burning or not, depends only on  $\phi(z)$  and the values of

$$M, \quad \varpi, \quad r_0, \quad (69)$$

as does also the value of  $p'$ .

For any one form of the function  $\phi(z)$  the functional relations here indicated are the same for all guns and propellants to which the equations (33), (38), (39) apply.

When  $\phi(z) = 1$ , and maximum pressure occurs during burning, we see from (67) that  $Mp'$  depends only on  $M\varpi$  and  $Mr_0$ , since for a concentrated band

$$\theta_1 = 1, \quad v_1 = 0, \quad z_1 = r_0.$$

Reverting now to the notation of § 8, we see that the solution of the equations of the gun, and in particular the value of

$$\frac{mu_1s_0}{(1-\beta)Av_0} V_3, \quad (70)$$

depend only on

$$\frac{(1-\beta) A^2 v_0^2}{kc \Pi m u_1^2 s_0^2}, \quad \frac{(C-c/\delta) u_0}{kc \Pi u_1}, \quad \frac{C-c/\delta}{kc \Pi} R_0, \quad \frac{C_3-c/\delta}{C-c/\delta}, \quad (71)$$

$C_3$  denoting the total capacity of the gun.

For the same propellant whose rate of burning is not proportional to the pressure, these may be replaced respectively by

$$\frac{m s_0}{(1-\beta) A v_0} \cdot V_3, \quad (70')$$

$$\text{and} \quad \frac{(1-\beta) A^2 v_0^2}{kc m s_0^2}, \quad \frac{C-c/\delta}{kc}, \quad R_0, \quad \frac{C_3-c/\delta}{C-c/\delta}. \quad (71')$$

When the charge is all burnt in the gun, then whether maximum pressure occurs during burning or not, and also the value of

$$\frac{C-c/\delta}{kc \Pi} P', \quad (72)$$

depend only on the values of

$$\frac{(1-\beta) A^2 v_0^2}{kc \Pi m u_1^2 s_0^2}, \quad \frac{(C-c/\delta) u_0}{kc \Pi u_1}, \quad \frac{C-c/\delta}{kc \Pi} R_0. \quad (73)$$

Again, for the same propellant whose rate of burning is not proportional to the pressure, these may be replaced by

$$P' \quad (72')$$

$$\text{and} \quad \frac{(1-\beta) A^2 v_0^2}{kc m s_0^2}, \quad \frac{C-c/\delta}{kc}, \quad R_0, \quad (73')$$

respectively.

If, further, the pieces of propellant have a constant burning surface, and maximum pressure occurs during burning, then

$$\frac{(1-\beta)(C-c/\delta)}{m} \left( \frac{A v_0}{kc \Pi u_1 s_0} \right)^2 P', \quad (74)$$

depends only on

$$\frac{(1-\beta)(C-c/\delta)}{m} \left( \frac{A v_0}{kc \Pi u_1 s_0} \right)^2 \frac{u_0}{u_1}, \quad \frac{(1-\beta)(C-c/\delta)}{m} \left( \frac{A v_0}{kc \Pi u_1 s_0} \right)^2 R_0. \quad (75)$$

One of the relations of this section has been used by F. B. Pidduck. Taking the same propellant with the rate of burning proportional to the pressure, so that  $u_0 = 0$ , we have that

$$\frac{(C-c/\delta)}{kc} P', \quad (72)''$$

depends only on

$$\frac{(1-\beta) A^2 v_0^2}{kc m s_0^2}, \quad \frac{(C-c/\delta)}{kc} R_0. \quad (73)''$$

Pidduck plotted observed values of the first of these three quantities against the second, and sought the effect of the third.

The method appears capable of much further utility. For example, on taking the same propellant and

$$\phi(z) = 1, \quad u_0 = 0,$$

we have, when maximum pressure occurs during burning

$$\frac{(1-\beta)(C-c/\delta)}{m} \left( \frac{A v_0}{k c s_0} \right)^2 P', \quad (74)'$$

depending only on

$$\frac{(1-\beta)(C-c/\delta)}{m} \left( \frac{A v_0}{k c s_0} \right)^2 R_0. \quad (75)'$$

But the greatest value of the present relations is when the rate of burning is not proportional to the pressure, and the equations of the gun cannot be integrated by elementary functions. For example, when with the same propellant

$$\phi(z) = 1, \quad u_0 \neq 0,$$

and when the maximum pressure occurs during burning,  $P'$  depends only on

$$\frac{(1-\beta)(C-c/\delta)}{m} \left( \frac{A v_0}{k c s_0} \right)^2, \quad R_0. \quad (75)''$$

*After Engraving with Rate of Burning Proportional to Pressure.*

12. We shall now take  $r = 0$ ,  $\pi = 0$ , and start from the conditions

$$\theta = \theta_1, \quad z = z_1, \quad v = v_1, \quad p = p_1.$$

From (50) and (52) we have

$$dv/dz = 1/\phi(z), \quad (76)$$

so that

$$v = v_1 + \int_{z_1}^z \frac{dz}{\phi(z)}, \quad (77)$$

and from (49) and (52) we have

$$p = \frac{Mv}{\phi(z)} \frac{dz}{d\theta}. \quad (78)$$

On substituting in (54) from (77) and (78) we obtain

$$\frac{1}{2}(\gamma-1) \frac{1}{\theta} \frac{d\theta}{dz} = \frac{v_1 + \int_{z_1}^z \frac{dz}{\phi(z)}}{\frac{2}{M} \left\{ \frac{z}{\gamma-1} - \int_1^{\theta_1} r d\theta \right\} - \left\{ v_1 + \int_{z_1}^z \frac{dz}{\phi(z)} \right\}^2} \cdot \frac{1}{\phi(z)},$$

giving

$$\log \left( \frac{\theta}{\theta_1} \right)^{\frac{1}{2}(\gamma-1)} = \int_{z_1}^z \frac{v_1 + \int_{z_1}^z \frac{dz}{\phi(z)}}{\frac{2}{M} \left\{ \frac{z}{\gamma-1} - \int_1^{\theta_1} r d\theta \right\} - \left\{ v_1 + \int_{z_1}^z \frac{dz}{\phi(z)} \right\}^2} \cdot \frac{dz}{\phi(z)}, \quad (79)$$

which is the general  $\theta, z$  relation after engraving and during burning.

For a concentrated band (77) and (79) reduce to

$$v = \int_{r_0}^z \frac{dz}{\phi(z)}, \quad (77)'$$

$$\text{and} \quad \log \theta^{\frac{1}{2}(\gamma-1)} = \int_{r_0}^z \frac{\int_{r_0}^z \frac{dz}{\phi(z)}}{\frac{2z}{(\gamma-1)M} - \left\{ \int_{r_0}^z \frac{dz}{\phi(z)} \right\}^2} \cdot \frac{dz}{\phi(z)}. \quad (79)'$$

The equations (77)' and (79)' form the basis of Charbonnier's solution, but in evaluating (79)' he approximates except for  $\phi(z) = 1$ .

On evaluating (79) for

$$\phi(z) = 1, \quad \phi(z) = (1-z)^{\frac{1}{2}},$$

we obtain

$$\frac{\theta}{\theta_1} = \left\{ \frac{b+2c\xi_1-\xi_1^2}{b+2c\xi-\xi^2} \right\}^{\lambda} \left\{ \frac{(a-c+\xi_1)(a+c-\xi)}{(a-c+\xi)(a+c-\xi_1)} \right\}^{\mu}, \quad (80)$$

with

$$a = (b+c^2)^{\frac{1}{2}},$$

where for  $\phi(z) = 1$ , or a constant burning surface,

$$\left. \begin{aligned} \xi &= z, & \xi_1 &= z_1, \\ b &= -\frac{2}{M} \int_1^{\theta_1} r d\theta - (z_1 - v_1)^2 \\ c &= 1/(\gamma-1)M + (z_1 - v_1) \\ \lambda &= 1/(\gamma-1) \\ \mu &= -1/(\gamma-1)^2 M a \end{aligned} \right\}, \quad (81)$$

and for  $\phi(z) = (1-z)^{\frac{1}{2}}$ , or cylindrical pieces of propellant,

$$\left. \begin{aligned} \xi &= (1-z)^{\frac{1}{2}}, & \xi_1 &= (1-z_1)^{\frac{1}{2}} \\ b &= \frac{1}{1+1/2(\gamma-1)M} \left\{ \frac{1}{2M} \left( \frac{1}{\gamma-1} - \int_1^{\theta_1} r d\theta \right) - (\xi_1 + \frac{1}{2}v_1)^2 \right\} \\ c &= \frac{\xi_1 + \frac{1}{2}v_1}{1+1/2(\gamma-1)M} \\ \lambda &= \frac{1}{\gamma-1+1/2M} \\ \mu &= \frac{2M}{a} \frac{\xi_1 + \frac{1}{2}v_1}{\{1+2(\gamma-1)M\}^2} \end{aligned} \right\}. \quad (82)$$

After all the charge is burnt, our equations reduce to those in general use.

The result for a concentrated band may be obtained very easily by putting

$$\theta = 1, \quad v_1 = 0, \quad z_1 = r_0 (\neq 0),$$

in (81) and (82), but the derivation of those for *no band* requires a limiting process, so that they are most easily obtained directly.

For  $\phi(z) = 1$  the results are given by Charbonnier,\* while for  $\phi(z) = (1-z)^{\frac{1}{2}}$  we have

$$v = 2\{1 - (1-z)^{\frac{1}{2}}\}, \quad (83)$$

$$\theta = [\tfrac{1}{2} - (\gamma-1)M + \{\tfrac{1}{2} + (\gamma-1)M\} (1-z)^{\frac{1}{2}}]^{-\frac{1}{\frac{1}{2}(\gamma-1)+1/4M}}, \quad (84)$$

$$p\theta = [z - 2(\gamma-1)M\{1 - (1-z)^{\frac{1}{2}}\}]. \quad (85)$$

### *The Harmonic Development of the Tide-generating Potential.*

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#### § 1. *Introduction.*

The harmonic development of the tide-generating potential is the basis of most work on tidal observations, and since 1883 the development given by Sir G. H. Darwin has been universally used and has been of remarkable value. But discrepancies between prediction and observation are serious and have been attributed to faulty "harmonic constants"; it has been assumed that if these were improved better predictions would be obtained, and it has also been tacitly assumed that it is only necessary to consider the harmonic constituents as given by Darwin. Recent work, however, especially at the Tidal Institute, has shown that when all the "Darwinian constituents" are removed from the tidal height there is a residue composed of constituents which are not included in his schedules. These are such that any slight improvements possible in the "constants" usually obtained are comparatively negligible.

The obvious course, therefore, was to make a more thorough development of the potential, and in view of the unknown nature of the residues great accuracy was obviously desirable, especially as the possibility of resonance has always to be considered. The development given in this paper, even if it proves to be needlessly thorough for practical tidal work, will cover the needs of research work, since it includes all terms whose coefficients (relatively to the greatest coefficient) are greater than 0.00010.

Darwin used the old lunar theory and referred everything to the orbit rather than to the ecliptic; his results are all given in the algebraic form, arithmetic being used only to decide what terms to omit. His development is a quasi-harmonic development because he retains factors in the coefficients

\* *Loc. cit.*, Chap. VII.



and terms in the arguments which are considered as constant over fairly long intervals of time, such as a year, but which are really slowly variable. The present method of development uses the results of the modern lunar theory and is essentially a numerical method throughout. The theoretical expansions for the longitude and latitude of the moon referred to the ecliptic, as given by Brown,\* have been used, and the development is truly harmonic. Ferrel's development, published in 1874, was also truly harmonic, but it included only the most important terms.

The new schedules of constituents, as compared with the old schedules, contain many terms which, for modern purposes, are too large to be ignored; this matter is dealt with in § 9, and Table VI gives a comparison of the main terms as given in the old and in the new schedules. It is of interest to note that J. C. Adams verified Darwin's work and carried out the development so as to include more terms, but this work does not seem to have been published.

One great aim of the author has been to reduce the subject to its very simplest form, and what credit is due for this must be equally shared with Prof. J. Proudman, for whose criticism and advice the author is deeply indebted.

A great deal of attention has been paid to the matters of notation and presentation of results; a prominent feature in both is the adoption of a special notation for the arguments, which is such that any argument is represented by a number and, what is very striking, if the terms in the expansions are arranged according to the argument-number, they are thereby automatically arranged according to "speed," which is very convenient.

The application of the new development to the analysis of observations and to predictions is not fully dealt with in this paper. Certain suggestions are made, however, concerning future practice.

## § 2. *Development of the Lunar Tide-generating Potential.*

Let	$E$ = mass of the earth	}	(1)
	$M$ = mass of the moon		
	$r$ = distance between centres of earth and moon		
	$1/c$ = mean value of $1/r$		
	$\rho$ = radius of earth at given place P		
	$\lambda$ = latitude of P		
	$L$ = longitude of P, west of Greenwich		
	$a$ = mean radius of earth		
	$g$ = mean value of gravitational acceleration		
and	$V$ = tide-generating potential due to the moon		

\* 'Monthly Notices Roy. Astron. Soc.,' vol. 65, p. 285 (1905).

Then

$$V = \frac{\mu M \rho^2}{r^3} \left( P_2 + \frac{\rho}{r} P_3 + \frac{\rho^2}{r^2} P_4 + \dots \right) = V_2 + V_3 + V_4 + \dots, \quad (2)$$

where  $P_2 = \frac{1}{2} (3 \cos^2 \vartheta - 1)$ ,

$P_3 = \frac{1}{2} (5 \cos^3 \vartheta - 3 \cos \vartheta)$ ,

$P_4 = \frac{1}{8} (35 \cos^4 \vartheta - 30 \cos^2 \vartheta + 3)$ ,

$\vartheta$  = geocentric zenith distance of the moon from P,

and  $\mu$  = attraction between unit masses at unit distance apart  
 $= g a^2 / E$ .

The ultimate result of the development of  $V$  is a series of terms harmonic in time, and as only the relative values of these are usually of importance, it is convenient to have the greatest numerical coefficient approximately unity; hence we write

$$G = \frac{3}{4} \frac{M}{E} \cdot \frac{g a^2 \rho}{c^3}, \quad (3)$$

and therefore

$$\left. \begin{aligned} V_2 &= \frac{3}{2} (3 \cos^2 \vartheta - 1) \cdot G (c/r)^3 \\ V_3 &= \frac{3}{2} (5 \cos^3 \vartheta - 3 \cos \vartheta) \cdot G (c/r)^4 (\rho/c) \\ V_4 &= \frac{1}{8} (35 \cos^4 \vartheta - 30 \cos^2 \vartheta + 3) \cdot G (c/r)^5 (\rho/c)^2 \end{aligned} \right\}. \quad (4)$$

The factor  $\rho/c$  is small and can be taken as equal to the value of the sine of the mean equatorial horizontal parallax, whose numerical value is  $3422''.70 \div 206265'' = 0.0165937$ .

The first stage in the further development of these functions is the separation of the long-period, diurnal, semi-diurnal, ter-diurnal, and quarter-diurnal species of constituents. Referring to fig. 1, let  $r$  be the first point of Aries,

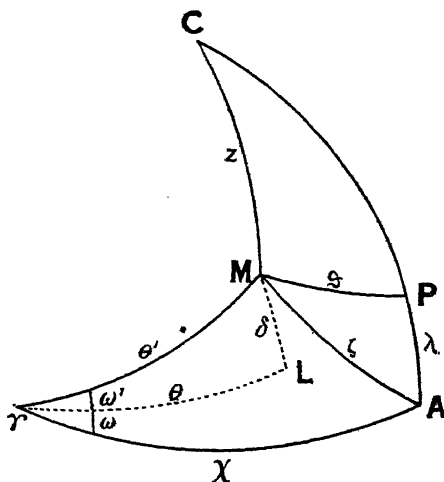


FIG. 1.

M the place of the moon, C the north Pole, P the given place, and A the intersection of the meridian of P with the equator,  $\gamma A$ . Also let  $\theta' z$ ,  $\mathfrak{z}$ ,  $\zeta$ , and  $\chi$  be respectively the geocentric zenith distances  $\gamma M$ ,  $MC$ ,  $MP$ ,  $MA$ , and  $\gamma A$ .

Then, from the spherical triangle MCP we have

$$\cos \mathfrak{z} = \sin \lambda \cos z + \cos \lambda \sin z \cos C,$$

and since the angle C increases at the rate of approximately  $360^\circ$  per mean lunar day, the expansion of  $V_2$ ,  $V_3$ , and  $V_4$  in terms of  $\cos C$ ,  $\cos 2C$ ,  $\cos 3C$ , and  $\cos 4C$  will separate the species of constituents; these expansions are expressed as series of terms involving functions of  $\lambda$  and  $G$ , multiplied by functions of  $z$  and  $C$ . The former will be called "geodetic coefficients," and it is desirable that these should all be expressed with the same maximum value,  $G$ , so that the numerical coefficients of the harmonic constituents ultimately obtained will give the chief index of their relative importance.

It is easy to verify, either directly, or by using the theory of spherical harmonics, that

$$\left. \begin{aligned} V_2 &= (c/r)^2 (G_0 H_0 & + & G_1 H_1 + & G_2 H_2) \\ V_3 &= (c/r)^3 (0.0044947 G_0' H_0' & + 0.011425 G_1' H_1' & + 0.031935 G_2' H_2' \\ & & + 0.013828 G_3' H_3') \\ V_4 &= (c/r)^4 (0.000046 G_0'' H_0'' & + 0.000121 G_1'' H_1'' & + 0.000148 G_2'' H_2'' \\ & & + 0.000522 G_3'' H_3'' & + 0.000201 G_4'' H_4'') \end{aligned} \right\} \quad (5)$$

where

$$\left. \begin{aligned} G_0 &= \frac{1}{2} G (1 - 3 \sin^2 \lambda) \\ G_1 &= G \sin 2\lambda \\ G_2 &= G \cos^2 \lambda \\ &\dots\dots\dots \\ G_0' &= 1.11803 G \sin \lambda (3 - 5 \sin^2 \lambda) \\ G_1' &= 0.72618 G \cos \lambda (1 - 5 \sin^2 \lambda) \\ G_2' &= 2.59808 G \sin \lambda \cos^2 \lambda \\ G_3' &= G \cos^3 \lambda \\ &\dots\dots\dots \\ G_0'' &= 0.12500 G (3 - 30 \sin^2 \lambda + 35 \sin^4 \lambda) \\ G_1'' &= 0.47346 G \sin 2\lambda (3 - 7 \sin^2 \lambda) \\ G_2'' &= 0.77778 G \cos^2 \lambda (1 - 7 \sin^2 \lambda) \\ G_3'' &= 3.07920 G \sin \lambda \cos^3 \lambda \\ G_4'' &= G \cos^4 \lambda \\ &\dots\dots\dots \end{aligned} \right\} \quad (6)$$

$$\begin{aligned}
H_0 &= \frac{2}{3} - 2 \cos^2 z \\
H_1 &= \sin 2z \cos C = 2 \cos z \cos \zeta \\
H_2 &= \sin^2 z \cos 2C = 2 \cos^2 \zeta - \sin^2 z \\
&\dots\dots\dots \\
H_0' &= \cos z (3 - 5 \cos^2 z) \\
H_1' &= \sin z \cos C (1 - 5 \cos^2 z) = \cos \zeta (1 - 5 \cos^2 z) \\
H_2' &= \sin^2 z \cos z \cos 2C = \cos z (2 \cos^2 \zeta - \sin^2 z) \\
H_3' &= \sin^3 z \cos 3C = \cos \zeta (4 \cos^2 \zeta - 3 \sin^2 z) \\
&\dots\dots\dots \\
H_0'' &= 3 - 30 \cos^2 z + 35 \cos^4 z \\
H_1'' &= \sin 2z \cos C (3 - 7 \cos^2 z) \\
H_2'' &= \sin^2 z \cos 2C (1 - 7 \cos^2 z) \\
H_3'' &= \sin^3 z \cos z \cos 3C \\
H_4'' &= \sin^4 z \cos 4C
\end{aligned}$$

The numerical factors in the geodetic coefficients are necessary for each coefficient to have the same maximum value.

The second forms of the expressions for  $H_1$ ,  $H_2$ ,  $H_1'$ ,  $H_2'$ , and  $H_3'$  are obtained by using

$$\sin z \cos C = \cos \zeta,$$

derived from the spherical triangle MCA. The corresponding expressions for  $H_0'' \dots H_4''$  are not given, simply because they are not used; obviously there are simple relations between these and  $H_0$ ,  $H_1$  and  $H_2$ , and those are used, as will be shown later.

The development in terms of  $\cos z$  and  $\cos \zeta$  is required in order to use the known harmonic expansions for the longitude and latitude of the moon referred to the ecliptic. Referring to fig. 1, let  $\gamma L$  be the ecliptic and let

$$\left. \begin{aligned}
\theta &= \gamma L = \text{longitude of moon} \\
\delta &= LM = \text{latitude of moon} \\
\omega &= \text{angle } A \gamma L = \text{inclination of ecliptic to equator} \\
\text{and } \omega' &= \text{angle } L \gamma M
\end{aligned} \right\} \quad (7)$$

Then we have

$$\begin{aligned}
\cos z &= \sin \theta' \sin (\omega + \omega'), \\
\cos \zeta &= \cos \theta' \cos \chi + \sin \theta' \sin \chi \cos (\omega + \omega'),
\end{aligned}$$

and

$$\cos \theta' = \cos \theta \cos \delta,$$

$$\sin \theta' \sin \omega' = \sin \delta,$$

$$\sin \theta' \cos \omega' = \sin \theta \cos \delta;$$

whence

$$\left. \begin{aligned}
\cos z &= \sin \omega \cos \delta \sin \theta + \cos \omega \sin \delta \\
\cos \zeta &= \cos \delta \cos \theta \cos \chi + (\cos \omega \cos \delta \sin \theta - \sin \omega \sin \delta) \sin \chi
\end{aligned} \right\} \quad (8)$$

It is, of course, possible to expand  $V_2$ ,  $V_3$ , and  $V_4$  in terms of  $\theta$  and  $\delta$  direct, but a good deal of analysis would be necessary; in addition to losing the present simplicity of the analysis, no real saving of arithmetical work would be achieved. The arithmetical expansions of  $\cos z$  and  $\cos \zeta$  are first obtained from the expressions of the longitude and latitude of the moon, and the rest of the work simply consists of carrying out systematically the operations involved in (5) and (6). The value of  $\omega$  used in (8) is the value on January 1, 1900, viz.,  $\omega = 23^\circ 27' 8'' \cdot 26$ .

### § 3. *Choice of Variables for Arguments.*

The expansions for  $V_2$  and  $V_3$  necessarily involve six independent variables in the arguments, and considerable attention has been paid to the choice of these. For reasons which will be appreciated later, the independent variables adopted are defined as follows:—

$$\left. \begin{aligned} \tau &= \text{local mean lunar time reduced to angle} \\ s &= \text{moon's mean longitude} \\ h &= \text{sun's mean longitude} \\ p &= \text{longitude of moon's perigee} \\ N' &= -N, \text{ where } N \text{ is the longitude of the moon's ascending node} \\ p_1 &= \text{longitude of sun's perigee} \end{aligned} \right\} \quad (9)$$

These are taken in preference to the variables ordinarily used in lunar theory.

Mean solar time will be taken as commencing at midnight, and, analogously, local mean lunar time will be measured from the lower transit of the "mean moon." Then, if we write

$$\left. \begin{aligned} t &= \text{Greenwich mean solar time} \\ \text{we have } \chi &= 15^\circ t + h - 180^\circ - L \\ \text{and } \tau &= \chi - s + 180^\circ = 15^\circ t + h - s - L \end{aligned} \right\} \quad (10)$$

At first sight the choice of  $t$  rather than  $\tau$  as an independent variable seems simpler, but there are many conveniences attached to the choice of the argument of the principal lunar constituent as one of the independent variables, both in the presentation of the schedules and in actual application.

The "speeds" of the variables are all positive, and, as they are written, are in descending order of magnitude. The chief variables are  $\tau$ ,  $s$ , and  $h$ , and it is a curious fact that if we classify in terms of  $\tau$ , with a sub-classification with regard to  $s$ , and a further sub-classification with regard to  $h$ , the constituents are completely separated into groups with no over-lapping of speeds. It is still more curious that to the order required the same process

can be continued for all the variables. Owing to this, a rather elegant and very useful form of presentation of the results is possible.

#### § 4. *Numerical Data for Arguments.*

The numerical data for the arguments is given by Brown, or may be obtained from the 'Nautical Almanac,' 1917 and 1923. The origin of time is taken as midnight at Greenwich on January 0-1, 1900 :—

$$\begin{aligned}\tau &= 15^\circ t + h - s - L, \\ s &= 277^\circ 0248 + 481267^\circ 8906T + 0^\circ 0020T^2 + \dots, \\ h &= 280^\circ 1895 + 36000^\circ 7689T + 0^\circ 0003T^2 + \dots, \\ p &= 334^\circ 3853 + 4069^\circ 0340T - 0^\circ 0103T^2 + \dots, \\ N' &= 100^\circ 8432 + 1934^\circ 1420T - 0^\circ 0021T^2 + \dots, \\ p_1 &= 281^\circ 2209 + 1^\circ 7192T + 0^\circ 0005T^2 + \dots,\end{aligned}$$

where T is a Julian century of 36,525 mean solar days.

The speeds per mean solar day are as follows :—

$$\begin{aligned}\dot{\tau} &= 360^\circ - 12^\circ 19074939, & \dot{p} &= 0^\circ 11140408, \\ \dot{s} &= 13^\circ 17639673, & \dot{N}' &= 0^\circ 05295392, \\ \dot{h} &= 0^\circ 98564734, & \dot{p}_1 &= 0^\circ 00004707.\end{aligned}$$

The speeds per mean solar hour are not very important, and are omitted.

No provision is made in this paper for the discussion of observations other than those referred to Greenwich mean solar time.

#### § 5. *The Argument-Number.*

The actual calculations have been facilitated very considerably by the use of a special notation for the arguments, and this notation has been retained in the schedules. All the arguments are linear functions of the standard variables, with integral coefficients, and it is very desirable to have a short method of writing such expressions as

$$2\tau - 3s + 4h + p - 2N' + 2p_1.$$

Now the various coefficients involved in the expressions for the arguments are only occasionally outside the range  $-4$  to  $4$ , and this suggests the use of a datum of five for each so as to avoid writing negative values as much as possible. In the case of  $\tau$ , however, the coefficients are always taken as positive, and with this exception, if we add five to each of the coefficients in the above expression we shall get the *argument-number*

$$229\cdot637.$$

This number will serve to denote the argument and may also be used to denote the term as a whole. It is divided into two parts for reasons explained later.

In rare instances the coefficients are outside the range  $-4$  to  $4$  and in these cases we replace  $-6$  by  $\bar{1}$ ,  $-5$  by  $0$ ,  $5$  by  $X$  and  $6$  by  $E$ . The addition (or subtraction) of arguments is quite simple; allowance has to be made for the datum  $055.555$ , which should be subtracted (or added) either before or after the operation—the former method is most convenient when dealing with the addition of one argument to each of a series of arguments.

### § 6. *Methods of Calculation.*

The original data for the longitude, latitude and sine parallax of the moon were obtained from the Tables by Brown, and are given in Tables I to III in the notation of § 3; the coefficients in the expansions of the longitude and latitude were reduced to radians, and the coefficients in the sine parallax expansion divided by the absolute term  $3422''.70$  in order to get  $c/r$ . In these expansions the coefficients are given to six decimal places.

The procedure is substantially that indicated by equations (8), (5) and (6). It may be noted that  $H_0$  and  $H_2$  can be calculated together, since

$$2 \cos^2 \zeta = H_2 + \frac{1}{2} H_0 + \frac{2}{3}.$$

In the case of the terms arising from  $V_3$ , the expansions of  $(c/r)^4 \cos z$  and  $(c/r)^4 \cos \zeta$  were determined and used as follows:—

$$(c/r)^4 H_0' = \left(\frac{4}{3} + \frac{5}{2} H_0\right) \cdot (c/r)^4 \cos z, \quad (c/r)^4 H_1' = \left(-\frac{2}{3} + \frac{5}{2} H_0\right) \cdot (c/r)^4 \cos \zeta,$$

$$(c/r)^4 H_2' = H_2 \cdot (c/r)^4 \cos z,$$

and

$$(c/r)^4 H_3' = \text{ter-diurnal part of } 2H_2 \cdot (c/r)^4 \cos \zeta.$$

The terms arising from  $V_4$  were found in a similar manner;  $4 \cos^4 z$  was obtained from  $(\frac{2}{3} - H_0)^2$  and hence  $H_0''$  was readily calculated; also we have

$$H_1'' = \left(\frac{2}{3} + \frac{7}{2} H_0\right) \cdot H_1,$$

$$H_2'' = \left(-\frac{4}{3} + \frac{7}{2} H_0\right) \cdot H_2,$$

$$H_3'' = \text{ter-diurnal part of } H_1 H_2,$$

$$H_4'' = \text{quarter-diurnal part of } \frac{1}{2} H_2^2.$$

The terms resulting from  $V_4$ , however, were, except for one term, just too small to be incorporated in the schedules.

The order of variables adopted in § 3 was not altogether the best for actual calculations and certain modifications were made. Brown's arguments for  $(\theta - s)$ ,  $\delta$  and  $c/r$  are given in the form

$$a(s-h) + b(s-p) + c(s-N) + d(h-p_1),$$

and if the variables be changed to  $s$ ,  $h$ ,  $p$ ,  $N$  and  $p_1$ , this expression takes the form

$$As + Bh + Cp + DN + Ep_1$$

with the relation  $A+B+C+D+E=0$ . If the datum 5 be used then the sum of the figures in each argument-number is 25.\*

Knowing this, it was possible to omit systematically one figure of the argument-number, and so to save a considerable amount of writing. In the case of  $\cos z$  and  $\cos \zeta$ , however, this relation was not the same for all terms, but they separated themselves into sets of which the characteristic was that the sum of the figures of an argument-number was constant within the set.

By rearranging the order of the variables the terms of a set were separated into large groups in which the only effective variables were  $s$  and  $h$ , if  $p$  be ignored as mentioned above. The advantage gained by grouping was enormous because of the amount of writing thereby eliminated, and in fact the calculations were greatly facilitated by these methods of grouping.

The actual multiplication of series was quite an easy matter, and very efficient current checks were available; the greatest trouble was in connection with the collection of coefficients contributing to a term in the expansion, and this part of the work was always done twice. The author acknowledges with thanks the great assistance he has received from the staff of the Tidal Institute in this laborious arithmetical work.

Certain methods of checking were used which may be illustrated from Table III. Consider the calculation of  $(c/r)^3$  from  $(c/r)$ ; if we suppose that all the variables are made zero except  $s$  then each of these expansions reduces to seven group-terms: all the coefficients of terms whose argument-numbers start with six would be added together, and so on. Taking the abbreviated expansion of  $(c/r)$  and cubing it should give an expansion for the abbreviated value of  $(c/r)^3$  whose terms should be equal to the group-terms obtained from the full expansion. This method of checking, with appropriate modifications, has been used with the groupings explained above, and it has been very efficient indeed. The difference between any two such group-terms obtained by the two methods has always been less than 0.000050; usually it has been much less than this. In the one case where the difference reached 0.000050 no error could be found, but as coefficients less than 0.000005 were ignored in this case the probability of serious error in any one term is not great. The coefficients in the final schedules are reduced to five decimals and terms with coefficients less than 0.00010 have been ignored; the figures given may be taken as accurate to within two in the last place.

The expansions of  $(c/r)^3$ ,  $(c/r)^4$ ,  $\cos z$  and  $\cos \zeta$  are contained in the following Tables:—

\* In the Tables, however, it should be noted that the variable there used is  $-N$ , and not  $N$ , so that the relation just mentioned does not hold.



Table I.—Expansion for the Longitude of the Moon: ( $\theta-s$ ).  
Coefficients of sines to six decimals.

Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.
55·654	5	555	-605	74·356	47	85·255	175
753	1	654	-138	455	-41	475	-219
775	6	65·356	-2	554	-119	86·254	-3
56·356	-12	455	0·109760	75·355	3728	91·755	3
455	90	554	87	454	6	90·556	9
554	-3243	653	-12	575	-1996	91·555	67
576	7	675	-192	76·354	-37	92·356	6
57·355	-1026	66·355	9	574	2	554	-1
553	-37	454	-532	77·155	-5	576	-2
575	-267	575	3	375	3	93·355	70
58·354	-42	67·255	-64	81·657	2	575	-28
574	-11	453	-6	855	1	94·354	-1
59·353	-1	68·254	-2	80·656	21	95·155	9
60·658	1	70·558	2	81·457	4	375	-19
61·635	1	756	13	655	186	595	2
657	36	71·557	40	82·456	71	XI·655	2
855	6	656	-1	555	2	XO·456	1
62·436	-2	755	149	654	-3	XI·455	10
535	-1	72·556	802	676	-2	675	-1
656	1000	655	-16	83·455	931	X3·255	5
755	-6	754	-2	675	-46	475	-5
63·435	-31	73·335	-2	84·256	3	X5·275	-2
457	13	357	1	355	-3	E1·355	1
556	-3	555	0·011490	454	-14		
655	0·022236	654	1	476	-1		
64·456	717	775	-3	575	1		

Table II.—Expansion for the Latitude of the Moon: ( $\delta$ ).  
Coefficients of sines to six decimals.

Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.
55·566	-4	544	-59	466	38	84·366	4
665	-4847	566	24	565	-26	465	-3
56·444	-25	65·345	154	664	-6	564	-6
466	4	565	0·089504	75·245	8	85·365	300
565	23	66·344	-2	465	4897	585	-31
664	-27	465	2	564	4	86·364	-3
57·245	-1	564	-31	665	-14	90·666	2
465	-808	67·365	-75	76·464	-26	91·445	2
655	1	585	-11	77·265	-7	665	15
58·464	-36	68·364	-3	465	-2	92·466	6
59·463	-1	70·646	3	80·546	2	93·465	73
61·547	5	71·645	32	766	1	685	-1
745	3	667	2	81·545	18	94·464	-1
62·546	144	72·446	9	567	2	95·265	19
645	-2	545	-2	765	12	485	-5
63·545	3024	666	43	82·566	39	X1·565	6
765	-8	73·445	162	665	-1	X3·365	7
64·346	1	665	967	83·345	10	X5·165	1
445	-3	74·444	-4	565	568	E1·464	1

Table III.—Expansions for  $(c/r)$ ,  $(c/r)^3$  and  $(c/r)^4$ . (Lunar.)

Coefficients of cosines to six decimals, except for  $(c/r)^4$ , where the coefficients are given to four decimals.

Argument-number.	$c/r$ coefficient.	$(c/r)^3$ coefficient.	$(c/r)^4$ coefficient.	Argument-number.	$c/r$ coefficient.	$(c/r)^3$ coefficient.	$(c/r)^4$ coefficient.
55·555	1·000000	1·004736	1·0095	74·356	37	167	3
654		7		455	-32	-143	-2
775		-34	-1	554	-88	-287	-4
56·455	4	-42	-1	75·355	2970	13442	210
554	-117	-318	-4	454	5	22	
57·355	-89	1463	32	575	-4	-48	-1
553	-3	-7		76·354	-30	-135	-2
575	-31	-105	-2	77·155	-4	-11	
58·354	-6	47	1	375	-3	-13	
574	-2	-6		81·855	1	6	
61·657	14	46	1	80·656	20	91	1
855	2	26	1	81·457	3	13	
62·656	422	1348	18	655	176	814	13
755	-3	-11		82·456	67	308	5
63·435	-14	-52	-1	555		-10	
457	6	19		654	-3	-14	
655	0·010025	31475	430	83·455	902	4189	66
64·456	337	1014	14	675	-3	-15	
555	-285	-866	-12	84·256	4	21	
654	-66	-208	-3	355	-3	-16	
65·455	0·054501	0·164395	2201	454	-14	-65	-1
554	44	133	2	85·255	182	1076	19
653	-6	-18		475		-4	
675	-209	-629	-8	86·254	-3	-16	
66·355	5	13		91·755	3	17	
454	-273	-846	-11	90·556	10	50	1
575	2	6		91·555	76	396	6
67·255	-35	-2	1	92·356	6	36	1
453	-3	-9		554	-1	-5	
475	-24	-77	-1	93·355	83	496	9
68·254	-1	-1		94·354	-1	-8	
70·756	9	43	1	95·155	12	85	2
71·557	27	83	1	X1·655	3	15	
755	109	513	8	X0·456	2	11	
72·556	561	1771	24	X1·455	13	79	1
655	-11	-41	-1	X2·256		3	
73·335	-1	-6		X3·255	7	52	1
555	8249	26580	367	X5·055		4	
775	-4	-18		E1·355	1	9	

Table IV.—Expansion for  $\cos z$ . (Lunar.)

Coefficients of sines to six decimals.

Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.
55.556	-17	566	22	675	-10	575	-5
566	-4	655	-10	74.444	-4	775	-2
653	-2	754	2	456	175	84.356	19
655	-21825	65.345	141	466	30	366	4
665	-4442	355	143	555	-119	455	-15
675	-39	456	-2	565	-24	465	-3
56.444	-23	555	0.395818	654	-33	554	-31
454	-70	565	82032	664	-6	564	-6
456	21	575	-795	75.245	7	85.355	1329
466	4	775	6	255	6	365	275
555	120	66.344	-2	455	21684	375	-3
565	21	354	-2	465	4488	454	2
654	-108	356	-3	475	-44	575	-5
664	-25	455	26	554	17	86.354	-16
57.455	-4518	465	2	564	4	364	-3
465	-741	554	-647	653	-2	87.155	-4
653	-2	564	-28	675	-82	90.656	8
675	12	576	2	685	-17	666	2
58.454	-198	67.355	-451	76.355	4	91.445	2
464	-33	365	-69	454	-142	655	64
59.453	-7	553	-7	464	-24	665	14
463	-5	575	-78	77.255	-39	92.456	25
61.557	7	585	-13	265	-6	466	6
745	3	68.354	-17	453	-2	93.455	326
755	5	364	-3	475	-13	465	67
62.536	2	574	-3	485	-3	675	-2
546	132	70.646	3	78.254	-2	94.256	2
556	142	71.645	29	80.546	2	355	-2
645	-2	655	12	756	5	454	-6
655	-2	657	7	81.545	17	95.255	86
63.535	32	667	2	555	4	265	17
545	2769	72.446	8	557	9	96.254	-2
555	2020	456	4	567	2	X0.556	3
557	8	545	-2	755	52	X1.555	26
755	-40	656	197	765	11	565	6
765	-7	666	39	82.556	176	X2.356	3
64.356	2	73.435	-5	566	36	X3.355	33
445	-3	445	149	655	-5	365	6
455	-2	455	57	83.345	9	X5.155	6
544	-54	457	3	355	3	E1.455	4
554	-17	655	4282	555	2528	E3.255	3
556	637	665	885	565	524		

Table V.—Expansion for  $\cos \zeta$ . (Lunar.)

Coefficients of cosines to six decimals.

Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.	Argument-number.	Coefficient.
107·855	7	655	52249	755	3	564	-6
109·655	11	146·456	-81	163·435	28	177·355	-47
115·955	13	545	5	457	-6	365	-15
117·755	79	555	-288	645	161	575	-8
118·754	7	644	-7	655	-10886	585	-3
119·555	63	654	422	164·446	5	180·656	-3
11X·554	8	147·445	-192	456	-261	181·645	6
11E·355	3	455	10818	545	-5	655	-29
124·856	-5	554	-3	555	290	182·456	-11
125·845	-4	653	8	654	50	555	-3
855	208	655	-6	656	7	656	20
126·656	-13	665	-32	666	5	666	9
755	-5	675	-11	165·435	4	183·445	32
854	5	148·355	-3	445	963	455	-138
127·435	-4	444	-9	455	-52590	655	444
645	-15	454	476	554	-42	665	192
655	786	149·453	17	653	6	675	23
128·456	-3	465	-6	655	-2264	184·456	18
654	60	152·536	-8	665	-963	466	7
129·445	-3	756	-40	675	94	555	-12
455	155	153·525	3	166·444	-5	565	-5
653	3	535	-187	454	168	654	-3
12X·454	18	557	-17	456	2	185·255	-14
133·955	-9	745	15	555	12	455	2250
134·756	-38	755	-1089	565	5	465	973
135·535	-12	154·534	6	654	-11	475	106
656	5	546	6	664	-5	675	-9
745	-60	556	-1559	167·455	-469	685	-4
755	3202	655	62	465	-161	186·454	-15
136·556	-75	754	-8	168·454	-21	464	-5
655	-35	155·335	13	464	-7	187·255	-4
754	46	535	83	171·557	-17	191·545	4
137·335	-4	545	-17788	755	-12	555	-10
545	-114	555	0·953747	172·546	29	755	5
555	6091	654	-5	555	-343	765	2
138·455	-12	755	-15	655	4	192·556	18
544	-8	765	-81	173·535	3	566	8
554	424	775	3	545	600	193·355	-8
139·345	-2	156·356	6	555	-4868	555	262
355	127	455	-24	755	-4	565	114
553	21	544	-5	174·356	-4	575	12
565	-4	554	1536	455	5	194·554	-3
13X·354	11	566	12	544	-12	195·355	138
142·356	-4	157·355	-96	554	42	365	60
143·635	-32	553	19	556	66	375	7
657	-4	555	-210	566	5	1X1·655	7
855	-94	565	-600	576	-3	665	3
144·646	5	575	77	175·345	31	1X2·456	3
656	-341	158·554	-15	355	-345	1X3·455	34
755	10	564	-29	555	41067	465	15
145·425	4	574	4	565	17788	1X5·255	9
435	-197	161·635	3	575	1916	265	4
457	-6	657	-17	176·354	4	1E1·555	3
556	42	855	3	455	3	1E3·355	3
635	5	162·646	7	554	-67		
645	-973	656	-477				

§ 7. *Development of the Solar Tide-generating Potential.*

The tide-generating potential due to the sun is developed by methods similar to those already used, but the whole problem is much simpler in this case. The expansions for the longitude and sine-parallax of the sun contain very few terms, and the sun's latitude may be ignored.

Using subscripts to denote quantities corresponding to those used for the lunar potential, we have

$$\left. \begin{aligned} \theta_1 &= h + 0.033501 \sin(h-p_1) + 0.000351 \sin 2(h-p_1) \\ &\quad + 0.000005 \sin 3(h-p_1) + \dots \\ c_1/r_1 &= 1 + 0.016750 \cos(h-p_1) + 0.000281 \cos 2(h-p_1) \\ &\quad + 0.000005 \cos 3(h-p_1) + \dots \end{aligned} \right\}, \quad (11)$$

which may be obtained from the formulæ of elliptic motion, with eccentricity 0.0167504.

The geodetic coefficients are the same as for the lunar potential, except that  $G$  is replaced by

$$G_1 = \frac{3}{4} \frac{S}{E} \frac{ga^2 p^2}{c_1^3} = \frac{S}{M} \frac{c^3}{c_1^3} G, \quad (12)$$

where  $S$ ,  $M$ ,  $E$  are respectively the masses of the sun, moon and earth. It is desirable, however, to retain  $G$  as the common coefficient of both lunar and solar constituents, and to absorb the factor  $(S/c_1^3) \div (M/c^3)$  in the numerical coefficients of the solar constituents. Now,  $1/c$  and  $1/c_1$  are proportional to the sines of the mean equatorial horizontal parallaxes of the moon and sun, respectively; the former is accurately known, and its value is  $3422''.70$ ; also, it is definitely known and well established\* that  $S/E$  multiplied by the cube of the mean equatorial horizontal parallax of the sun, is equal to  $2''26428 \times 10^9$ . The mass of the moon is not very accurately known, but the best value† is apparently given by  $E/M = 81.53 \pm 0.047$ . We therefore obtain  $G_1 = 0.46040 G$ , and this numerical coefficient has been used.

The terms arising from the solar potential are given in the same schedules as those arising from the lunar potential, and are distinguished by inserting the appropriate geodetic coefficient for the solar terms, and leaving it as understood for the lunar terms.

§ 8. *Explanation of the Schedules.*

The harmonic terms in the development of the potential are contained in four schedules, numbered 0 to 3. The number of the schedule denotes the species; for example, Schedules 1 and 2 contain respectively all the diurnal and semi-diurnal terms, whatever be their source—lunar or solar,  $V_2$  or  $V_3$ .

\* Ball, 'Spherical Astronomy,' pp. 309 and 310.

† 'Monthly Notices, Roy. Astron. Soc.,' February, 1911.

Each term has a numerical coefficient and a geodetic coefficient, and the source of the term is indicated by the latter; terms arising from the lunar  $V_3$  have geodetic coefficients  $G_0'$ ,  $G_1'$ ,  $G_2'$  or  $G_3'$ , the suffix indicating the species. Terms arising from the solar  $V_2$  have geodetic coefficients  $G_0$ ,  $G_1$  or  $G_2$ , and so have the terms from the lunar  $V_2$ : to distinguish between the two sources, the geodetic coefficient is not written in the schedules for the lunar  $V_2$  terms, and at the top of each schedule is a note stating the geodetic coefficient that is supposed to be understood. The values of the geodetic coefficients, considered as functions of the latitude, are placed at the top of the schedule.

With each geodetic coefficient is associated either a sine or a cosine of the given argument; the necessary information is given at the top of the schedule; as examples, from Schedule 1 we have the terms

$$0.37689 G_1 \sin \{145.555\}, \quad -0.16817 G_1 \sin \{165.555\}$$

and  $-0.00108 G_1' \cos \{145.655\},$

and from Schedule 2 we have terms

$$0.90812 G_2 \cos \{255.555\}, \quad 0.42286 G_2 \cos \{273.555\}$$

and  $0.000525 G_2' \sin \{265.555\},$

curl brackets being used to denote the argument corresponding to the argument-number.

The numerical coefficients are given to five decimal places, and all terms with numerical coefficients less than 0.00010 are ignored. The latter rule just cuts out all the  $V_4$  terms except one, a quarter-diurnal term, which has a coefficient of 0.00016, and this also is ignored.

As was mentioned in § 3, the terms, when arranged according to the argument-number, are thereby automatically arranged according to speed, as may be easily verified from the speeds given in § 4. The full argument-number will be used to denote the associated term.

Considered from the point of view of analysis of tidal observations, and assuming that the terms in the tide correspond to the terms in the potential, it is possible, using one year's observations only, to distinguish between terms whose arguments differ by multiples of  $h$ , but not between terms whose arguments differ by multiples of  $p$ ,  $N'$  or  $p_1$ . If, therefore, we have several terms whose arguments are the same so far as  $\tau$ ,  $s$  and  $h$  are concerned, these must necessarily be regarded as one *constituent*.\* The

\* It is possible to infer the separate terms of a constituent if it be assumed that the harmonic terms in the tide have to one another the relations of corresponding terms in the potential, but this is a matter which hardly concerns us at the moment: the point is, that in actual analysis of records not exceeding one year, terms such as the above must be regarded as one.

word "constituent" will be applied and restricted to a set of terms wholly inseparable within a year; we can therefore appropriately speak of the first three figures of the argument-number as the "constituent-number," and it is convenient to apply the term "group-number" to the first two figures of the argument-number; as an example, take the following:—

argument-number : 265·555,  
 constituent-number : 265,  
 group-number : 26,  
 species-number : 2, *i.e.*, semi-diurnal.

It is impracticable, even were it desirable, to invent for each constituent a symbol corresponding to the symbols already in use; the constituent-number is much more serviceable than an initial can be, and it certainly conveys a great deal more. Certain symbols such as  $M_2$ ,  $S_2$ ,  $K_1$  and  $O_1$  are, however, well established, and may still be used. A list of Darwin's symbols, together with the corresponding constituent-number, is given later (Table VI). It should be remarked, however, that each tidal-constituent given by Darwin only includes a particular set of terms from the whole of the contributory terms to our constituents. Since, however, it is the same constituent that is dealt with, though his expression for it is not complete, there is no objection to regarding his symbols and our numbers as equivalent.

Two diagrams are given to illustrate the schedules. The first, Diagram A,

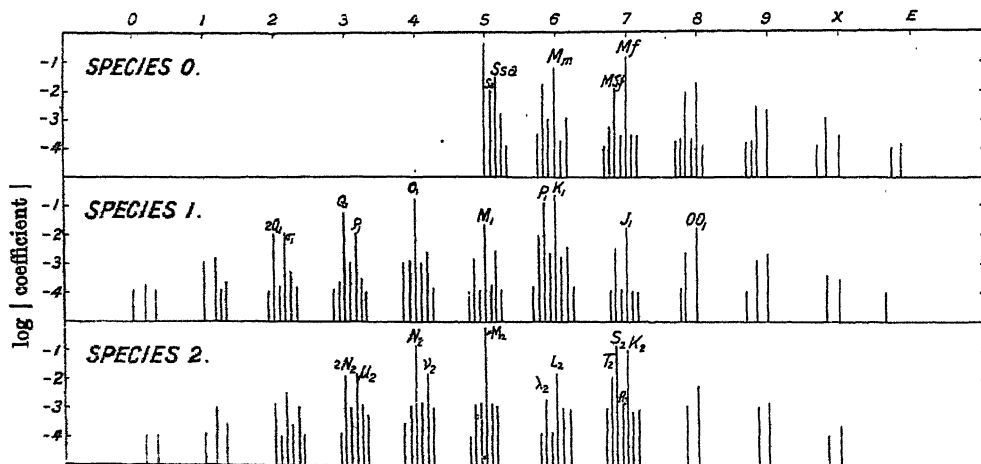


DIAGRAM A : constituents, separable in one year.

The speed scale is indicated by the figures at the top of the diagram; these, with the species-number, give the group-numbers, and the places of the constituents in the diagram can then be readily found. An increment of 1 in the group-number corresponds to an increase in speed of about  $13''$  per mean solar day; the increase in speed for an increase of 1 in the constituent-number is about  $1''$  per mean solar day.

gives for the first three species a representation of the constituents, with speed as abscissa and the logarithm of the absolute value of the coefficient as ordinate, assuming that the contributory terms are additive regardless of sign. The logarithmic scale gives, to some extent, a false idea of the magnitude of the constituent, but the scale is convenient for representation; further, the difficulties of analysis are not caused by the large constituents, but by the small ones, and, from this point of view, the logarithmic scale does correspond roughly to the difficulties experienced by the harmonic analyses.

Diagram B gives, on a more open scale than Diagram A, a representation of constituents separable in a period of about nineteen years. Terms whose

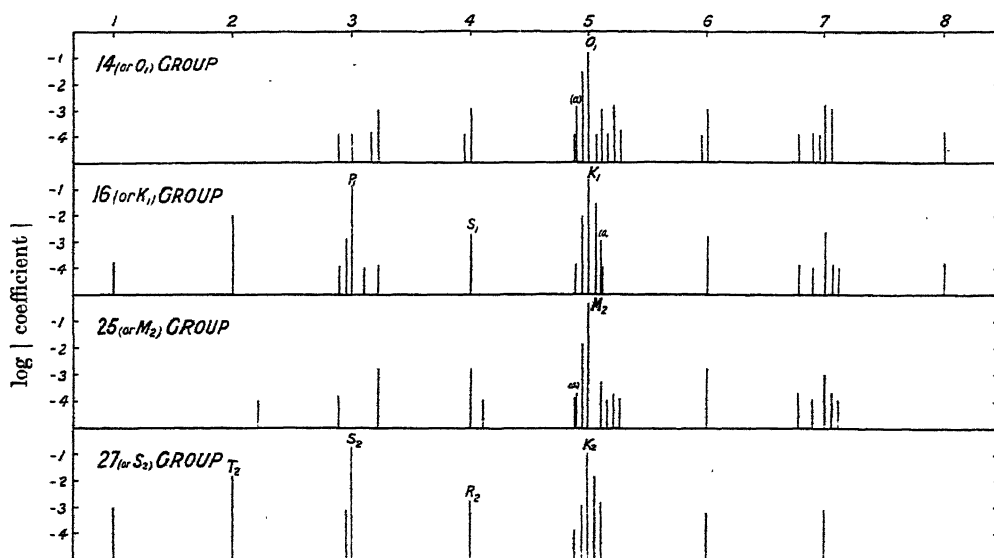


DIAGRAM B: terms separable in about nineteen years. (a): two distinct terms not separable from one another (see § 7).

The speed scale is indicated by the figures at the top of the diagram; these, with the group-number, give the constituent-number, and an increment of unity in constituent-number corresponds to an increment in speed of nearly  $1^\circ$  per mean solar day.

arguments differ only in  $p_1$  are regarded as one; in a few cases two terms may have nearly the same speed, though their arguments differ in  $p$  and  $N'$ , as in the case of the two terms 145.455 and 145.535. The speed of the latter term is greater than that of the former by  $\dot{p} - 2\dot{N}'$ , which is comparatively small; these terms are marked by (a) on the diagram. Only four groups are illustrated.



## SCHEDULE O.

$G_0 = \frac{1}{2}G(1-3\sin^2\lambda)$ , associated with coefficients of cosines to five decimals.

$G_0' = 1.11803 G \sin\lambda (3-5\sin^2\lambda)$ , associated with coefficients of sines to five decimals.

(When no geodetic coefficient is entered  $G_0$  is understood.)

Argument-number.	Coefficient.		Argument-number.	Coefficient.		Argument-number.	Coefficient.	
05 (or Ssa) group.			07 (or Mf) group.			08 group—contd.		
055·555	50458	$G_0$	071·755	26	$G_0'$	085·255	54	$G_0'$ $G_0'$
555	23411		072·556	91		455	2995	
565	-6552		073·545	98		465	1241	
575	64	$G_0'$	555	1370	$G_0'$	475	117	$G_0'$ $G_0'$
655	26		565	-88		555	38	
056·554	-16		655	15		565	24	
554	1176	$G_0$	074·554	-17	$G_0'$	675	-12	$G_0'$ $G_0'$
556	-61	$G_0$	556	48		086·454	-26	
057·355	73	$G_0$	566	12		09 group.		
553	30		075·345	-36	$G_0'$ $G_0'$	091·555	20	$G_0'$
555	12		355	677		755	14	
555	7287	365	-44	092·556		32		
565	-181	$G_0$	455	76	$G_0'$	566	13	$G_0'$
575	-40		465	12		093·355	25	
058·554	427		555	15642		555	478	
059·553	17	$G_0$	565	6481	565	200	$G_0'$	
06 (or Mm) group.			575	607	575	19		
062·656	68	$G_0'$ $G_0'$ $G_0'$	585	-13	095·355	396		
063·445	-16		076·554	-54	365	165		
645	-113		564	-14	375	16		
655	1578	$G_0'$	077·355	-47	455	11	$G_0'$	
665	-103		365	-19	0X group.			
064·456	51		08 group.			0X1·655		23
555	-44	$G_0'$	081·655	42	0X3·455	116		
654	-10		082·456	16	465	48		
065·445	-542		656	26	0X5·255	45		
455	8254	$G_0'$ $G_0'$ $G_0'$	666	11	265	19	$G_0'$	
465	-535		083·445	22	0E group.			
545	-24		455	217	0E1·555	12		
555	436	$G_0'$	465	-14	0E3·355	19		
565	73		555	13				
655	-442		655	569				
665	-179	$G_0'$	665	236				
675	-47		675	21				
066·454	-43		084·456	28				
067·455	-116	$G_0'$	466	10				
465	-58		555	-16				

## SCHEDULE I.

$G_1 = G \sin 2\lambda$ , associated with coefficients of sines to five decimals.

$G_1' = 0.72618G \cos \lambda (1 - 5 \sin^2 \lambda)$ , associated with coefficients of cosines to five decimals.

(When no geodetic coefficient is entered  $G_1$  is understood.)

Argument-number.	Coefficient.		Argument-number.	Coefficient.		Argument-number.	Coefficient.	
10 group.			13 (or $Q_1$ ) group—contd.			15 (or $M_1$ ) group.		
105.955	11		135.435	-28		152.656	-14	
107.755	46		545	-84	$G_1'$	153.645	-63	
109.555	28		555	-211	$G_1'$	655	-278	
			635	-42		154.656	15	
			645	1360		155.435	17	
			655	7216		445	-197	
			755	-13	$G_1'$	455	-1065	
			855	-19		545	98	$G_1'$
			136.456	-13		555	-661	$G_1'$
			555	-39		565	86	$G_1'$
			644	11		645	85	
			654	68		655	-2964	
			137.445	258		665	-594	
			455	1371		675	17	
			555	-18	$G_1'$	156.555	16	
			655	-78		654	-18	
			665	24		157.445	16	
			138.444	11		455	-566	
			454	64		465	-124	
			139.455	-14		158.454	-24	
11 group.			14 (or $O_1$ ) group.			16 (or $K_1$ ) group.		
115.755	-10	$G_1'$	143.535	-17		161.557	42	$G_1$
845	21		745	-20		162.556	1029	$G_1$
855	108		755	-113		163.535	14	
117.555	-10	$G_1'$	144.546	-15		545	-199	
645	53		556	-130		555	30	
655	278		145.455	12	$G_1'$	555	17554	$G_1$
118.654	21		535	-218		557	-11	$G_1$
119.445	10		545	7105		755	-26	
455	54		555	37689		164.554	-147	$G_1$
			645	16	$G_1'$	556	-423	$G_1$
			655	-108	$G_1'$	165.455	-36	$G_1$
			665	14	$G_1'$	545	1050	
			755	-243		555	-16817	$G_1$
			765	-40		555	-36233	
			146.544	12		565	-7182	
			554	115		575	154	
			147.355	-21	$G_1'$	655	-13	$G_1'$
			455	-21		166.554	-423	$G_1$
			545	14		167.355	-26	
			555	-491		563	-11	$G_1$
			565	107		555	-756	$G_1$
			148.554	-33		565	29	
						575	14	
						168.554	-44	$G_1$
12 group.								
124.756	-13							
125.645	-23	$G_1'$						
655	-58	$G_1'$						
745	180							
755	955							
126.556	-16							
655	-11							
754	15							
127.455	-11	$G_1'$						
545	218							
555	1153							
128.544	14							
554	79							
129.355	35							
13 (or $Q_1$ ) group.								
133.855	-23							
134.656	-61							

SCHEDULE 1—*continued.*

Argument-number.	Coefficient.		Argument-number.	Coefficient.		Argument-number.	Coefficient.
17 (or $J_1$ ) group.			18 (or $OO_1$ ) group.			19 group— <i>contd.</i>	
172·656	-24	$G_1'$	182·556	-32	$G_1'$ $G_1'$	195·255	-19
173·445	-17		183·545	-16		455	-311
645	18		555	-492		465	-199
655	-566		565	-96		475	-42
665	-112		185·355	-240		1X group.	
765	-89		365	-48		1X3·555	-50
174·456	-18		455	-40		565	-32
555	16		465	-16		1X5·355	-41
175·445	87		555	-1623		365	-27
455	-2964	$G_1'$	565	-1039	1E group.		
465	-587		575	-218	1E3·455	-12	
475	13		585	-14			
555	-241		19 group.				
655	46		191·655	-15			
665	29		193·455	-78			
675	17		465	-15			
176·454	15		655	-59			
177·455	12		665	-38			

## SCHEDULE 2.

$G_2 = G \cos^2 \lambda$ , associated with coefficients of cosines to five decimals.

$G_2' = 2.59808 G \sin \lambda \cos^2 \lambda$ , associated with coefficients of sines to five decimals.

(When no geodetic coefficient is entered  $G_2$  is understood.)

Argument-number.	Coefficient.		Argument-number.	Coefficient.		Argument-number.	Coefficient.		
20 group.			22 group— <i>contd.</i>			24 (or N <sub>2</sub> ) group.			
207·855	15		228·654	54		243·685	—15		
209·655	18		229·455	130		855	—56		
			22X·454	15		244·656	—147		
21 group.			23 (or 2N <sub>2</sub> ) group.			245·435	—63		
215·955	27		234·756	—31	G <sub>2</sub> '	545	—97	G <sub>2</sub> '	
217·755	111		235·535	—14		555	—569		
219·555	69		645	—27		556	14		
			655	—156		645	—648		
			745	—86	655	17387			
			755	2301	755	11	G <sub>2</sub> '		
22 group.			236·556	—40	246·456	—33			
225·755	—27	G <sub>2</sub> '	655	—25	555	—94			
855	259		754	36	654	163			
226·656	—12	G <sub>2</sub> '	237·455	—29	G <sub>2</sub> '	247·445	—123	G <sub>2</sub> '	
227·555	—27		545	—104		455	3303		
645	—25		555	2777		555	15		
655	671		238·554	189		655	17		
			239·355	85		665	—12		
						248·454	153		

## SCHEDULE 2—continued.

Argument-number.	Coefficient.		Argument-number.	Coefficient.		Argument-number.	Coefficient.	
25 (or $M_2$ ) group.			26 (or $L_2$ ) group—contd.			28 group.		
252·756	-11	$G_2'$	265·445	95	$G_2'$	283·655	123	$G_2'$
253·535	-40		455	-2567		665	54	
755	-273		545	-31		285·445	-12	
254·556	-314		555	525		455	643	
655	14		565	99		465	280	
255·455	32		645	-12		475	30	
535	47		655	643		555	48	
545	-3386		665	233		565	31	
555	·90812		675	40				
655	86		267·455	123				
665	16	465	59					
755	53	$G_2'$	27 (or $S_2$ ) group.			29 group.		
765	19		271·557	101	$G_2$	293·555	107	$G_2$
256·554	276		272·556	2479		565	46	
257·355	-52		273·545	94		295·355	53	
455	17		555	·42286		365	23	
555	107		555	72		555	168	
565	-51		274·554	-354		565	146	
575	18		556	92		575	47	
26 (or $L_2$ ) group.			275·455	29		2X group.		
262·656	-33	$G_2$	545	-147		2X3·455	17	$G_2$
263·645	24		555	7858		2X5·455	32	
655	-670		555	3648		465	28	
264·456	-10		565	3423				
555	17		575	372				
			276·554	92				
			277·555	98				

## SCHEDULE 3.

 $G_3' = G \cos^3 \lambda$ , associated with coefficients of cosines to five decimals.

Argument-number.	Coefficient.		Argument-number.	Coefficient.		Argument-number.	Coefficient.	
32 group.			34 group.			36 group.		
327·655	-17	$G_3'$	345·645	18	$G_3'$	363·655	17	$G_3'$
33 group.			655	-326	$G_3'$	365·455	67	$G_3'$
			347·455	-61	$G_3'$	655	-25	$G_3'$
			35 group.			37 group.		
335·755	-56	$G_3'$	355·545	66	$G_3'$	375·555	-155	$G_3'$
337·555	-57	$G_3'$	555	-1188	$G_3'$	565	-68	$G_3'$

§ 9. *Comparison with Darwin's Results.*

Darwin's schedules are not directly comparable with those now given, as his expansion is not purely harmonic. The constituents he gives are of the general form  $J \cos(\sigma t + u)$ , where  $\sigma$  is the appropriate speed,  $J$  is a function of the inclination of the moon's orbit to the equator, and  $u$  depends upon the position of the intersection of the equator and orbit.

Darwin's practice is to replace  $J$  and  $u$  by their mean values within the interval of time considered, and each set of observations is treated with different values of  $J$  and  $u$ . His theoretical "mean coefficient" is the mean value of  $J \cos u$  over a period of about nineteen years, the period of revolution of the node. He shows that  $J \cos(\sigma t + u)$  can be expanded in the form

$$\Sigma J_r \cos(\sigma t + r\Omega),$$

where  $\Omega$  is the longitude of the node;  $J_r$  is not quite constant, but partly depends upon the longitude of the node and upon the inclination of the orbit to the ecliptic. Darwin's mean coefficient is taken as equal to  $J_0$  in the above expansion. (This is not the mean value of  $J$ , however, which is somewhat larger than  $J_0$ : his theory and practice are not quite in conformity in this respect.)

Further expansion by the above method would be very difficult, but it can be shown that one of Darwin's constituents would yield ultimately a set of terms whose arguments would be identical, but for the part dependent on  $N'$ . On looking through the new schedules, such sets of terms can be readily picked out; the greatest numerical coefficient in each set should be very nearly equal to  $J_0$ , or Darwin's mean coefficient. It will be noticed, however, that in some cases several such sets of terms may be contributory to a "constituent" as defined in § 8. In all cases only one coefficient, the greatest, is extracted to represent each set, and in Table VI those terms (or representative terms) with coefficients greater than 0.00400 are set forth for comparison with Darwin's results. The constituent-number only is given to represent the argument. In those cases where Darwin has compounded two terms to form one constituent the comparison is made separately; the compounded terms are bracketed. In the case of  $M_1$  three terms are given, of which two are compounded by Darwin; the third term is the true  $M_1$ .

Generally speaking, there is fair agreement, except in the case of  $\mu_2$  and the true  $M_1$ ; the cause of the latter discrepancy has been ascertained to be due to certain approximations made by Darwin in expanding  $V_3$ .

The constituents omitted by Darwin and indicated in Table VI are considered to be decidedly worthy of consideration; their combined effect is by no means negligible.

Table VI.—Comparison of New Expansion with Darwin's.

Name.	Number.	Coefficient.	Darwin's coefficient.	Per cent. difference.
	055	0·50458	0·50448	0·0
Mf	075	0·15642	0·15654	0·1
Mf	075	677		
Mm	065	0·08254	0·08272	0·2
Mm	065	466		
Mm	065	—442		
Ssa	057	0·07287	0·07286	0·0
Ter-mensual	085	0·02995	0·03032	1·2
Evect. mthly.	063	0·01578	0·01510	4·3
Msf	073	0·01370	0·01242	9·3
Sa	056	0·01176		
	083	0·00569		
	093	0·00478		
	058	0·00427		
O <sub>1</sub>	145	0·37689	0·37712	0·1
K <sub>1</sub>	165	—0·36233	—0·36230	0·0
K <sub>1</sub>	165	—0·16817	—0·16814	0·0
P <sub>1</sub>	163	0·17554	0·17550	0·0
Q <sub>1</sub>	135	0·07216	0·07302	1·2
M <sub>1</sub>	155	—0·02964	—0·02970	0·2
M <sub>1</sub>	155	—0·01065	—0·01044	2·0
M <sub>1</sub>	155	—661	—0·00990	49·8
J <sub>1</sub>	175	—0·02964	—0·02970	0·2
OO <sub>1</sub>	185	—0·01623	—0·01624	0·0
$\rho_1$	137	0·01371	0·01416	3·3
$\sigma_1$	127	0·01153	0·00900	21·9
	162	0·01029		
2Q <sub>1</sub>	125	0·00955	0·00974	2·0
	167	—0·00756		
	173	—0·00566		
	183	—0·00492		
	147	—0·00491		
S <sub>1</sub>	164	—0·00423		
	166	—0·00423		
M <sub>2</sub>	255	0·90812	0·90852	0·0
S <sub>2</sub>	273	0·42286	0·42274	0·0
N <sub>2</sub>	245	0·17387	0·17592	1·2
N <sub>2</sub>	245	—569		
K <sub>2</sub>	275	0·07858	0·07858	0·0
K <sub>2</sub>	275	0·03648	0·03646	0·1
$\nu_2$	247	0·03303	0·03412	0·3
$\mu_2$	237	0·02777	0·02188	21·2
L <sub>2</sub>	265	—0·02567	—0·02574	0·3
L <sub>2</sub>	265	643	646	0·5
L <sub>2</sub>	265	525		
T <sub>2</sub>	272	0·02479	0·02486	0·3
2N	235	0·02301	0·02346	2·0
$\lambda_2$	263	—0·00670	—0·00660	1·5
	227	0·00671		
	285	0·00643		
M <sub>3</sub>	355	—0·01188	—0·01198	0·8

The effect of taking mean values of  $J$  and  $u$  over a period of a year is readily investigated; the process is practically equivalent to taking a mean value of  $N'$  (or  $N$ ) in the set of terms obtained by expanding  $J \cos(\sigma t + u)$ .

Suppose that

$$J \cos(\sigma t + u) = J_0 \cos \sigma t + J_1 \cos(\sigma t + N) + \dots;$$

then, if bars denote mean values of functions of  $N$ , we have

$$\begin{aligned} J \cos(\sigma t + u) - \bar{J} \cos(\sigma t + \bar{u}) &= J_1 \cos(\sigma t + N) - J_1 \cos(\sigma t + \bar{N}) \\ &= 2J_1 \sin \frac{1}{2}(\bar{N} - N) \sin(\sigma t + \frac{1}{2}N + \frac{1}{2}\bar{N}). \end{aligned}$$

Therefore the effect is to leave a residual harmonic term with coefficient approximately equal to  $J_1 \sin(\bar{N} - N)$ ; at the ends of the yearly period this has the approximate value of  $\frac{1}{2}J_1$ . Now the size of  $J_1$  is not to be judged by the size of  $J_0$ , and large residues may be left by the smaller constituents. On looking through the schedules it will be found that there is a possibility of residuals of coefficients 0.011, 0.005, 0.005, ..., in the long-period constituents, 0.012, 0.012, ..., in diurnal constituents, and 0.006, ..., in semi-diurnal constituents. These residues are by no means negligible, especially when there are other constituents of this order which are not taken into account; the total effect of these may be important.

#### § 10. *Considerations regarding Application to the Analysis and Prediction of Tides.*

The application of the schedules to the analysis and prediction of tides requires mature consideration, though it has been borne in mind during their preparation. In Darwin's paper on the abacus, he gives a method of analysis of the solar constituents which may be applied more generally. Essentially he regards the constituents of the 27 (or  $S_2$ ) group over a short interval of time as one constituent, and afterwards separates the various constituents  $T_2, S_2, R_2, K_2, \dots$  by considering the variations in certain quantities derived by harmonic analysis. This method may be generalised with considerable advantage. Considering each constituent as effectively a function of  $\tau, s$  and  $h$  only will simplify the application of such a method as this; it ought to simplify most methods.

If the variables  $p, N'$ , and  $p_1$  were absent, we should get constant coefficients for the constituents; actually their coefficients and arguments will vary very slowly, and it would probably be sufficient to tabulate for January 1 of each year the appropriate multiplying factor and change of phase; this would be a generalised form of  $J \cos(\sigma t + u)$ , as given by Darwin. But, for reasons already given, mean values over long periods are inadmissible; if, however, the multiplying factor and phase-shift be changed slowly but discontinuously at short intervals of time, the errors may be made negligible. Linear interpolation in  $J$  and  $u$  should suffice for this purpose. There seems to be no difficulty in doing this, either in analysis or in prediction.

Referring to the constituent 265, the chief term is  $265\cdot455$ , whose speed differs by  $\dot{p}$  from the speed of  $265\cdot555$ ; but there is no reason why the speed of the constituent 265 should be modified on this account, as any correction necessary would be automatically applied in using the variable coefficients and phases as indicated above.

To sum up, it is proposed—

(1) that the constituents be regarded as functions of  $\tau$ ,  $s$ , and  $h$ , with appropriate speeds;

(2) that analyses and predictions should be made with variable coefficients and phase corrections, automatically applied if possible, such coefficients and phase corrections being regarded as constants only over a sufficiently short interval of time.

The translation of these proposals into practical methods, however, is a matter for careful consideration.

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*The Production of Single Crystals of Aluminium and their  
Tensile Properties.*

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[PLATES 9-12.]

The crystals of which metals and alloys are composed are allotriomorphic. They are generally very small, and cannot usually be distinguished without the aid of a microscope. It is quite true that in the case of large castings weighing many tons, crystals of several cubic inches' capacity may be formed under special conditions of cooling. These, however, are quite rare, and possess the well-known dendritic or skeleton form. The majority of metals and alloys which have been hot-worked, have from 150 to 300 crystals to the linear inch, but frequently the size is still smaller, especially in steel. Rosenhain and Humphry\* counted the number of crystals in a known area of mild steel, and from that calculated the areas of individual crystals. The figures they give are from  $1\cdot5$  to  $7\cdot5 \times 10^{-6}$  square inches, according to the condition of the steel. Sykes† has recently given as the diameters of

\* 'Journ. of the Iron and Steel Inst.,' vol. 87, No. 1, p. 253 (1913).

† 'Bulletin of the American Inst. of Mining and Metallurgical Engineers,' February, 1921.



crystals in molybdenum wire figures varying from 0.0011 to 0.0002 of an inch in diameter. These correspond to approximately from 1000 to 5000 crystals to the linear inch. Admittedly, in this case, the wire was severely worked.

Sauveur\* was one of the first investigators to show that by carefully straining and subsequently heating such metals, crystals of a much larger size could be produced, and suggested that there was a critical stress which produced the largest crystals.

Subsequently, Rüder,† Chappell,‡ Jeffries§ and Hanson|| have shown that if a metal is locally deformed, and then heated, exceptionally large crystals form at some distance from the point at which the stress is the severest. If a tapered test-piece is used, a strain gradient is obtained, and it is found that the largest crystals always form within the strained region, but further from the area of greatest strain the higher the temperature. In his experiments, Rüder strained strips of silicon-steel sheet to various extents, and found that the largest crystals were formed on heating after a certain deformation, but that as this was exceeded the crystals become gradually smaller. Seligman and Williams¶ stretched aluminium sheet, which had previously been heated, to various degrees, and found, on heating, that up to a certain point, a small deformation had no effect. Beyond this point, however, large crystals were formed, and, as the deformation was further increased, the crystal size was diminished. The crystals produced by these methods were very large compared with those in the original metal, some of them being 0.5 of an inch long.

In recent years wires have been produced, both of tungsten and molybdenum, in which the crystals occupy the entire cross-section of the wire. Indeed, considerable lengths of tungsten wire are now made for lamp filaments, which are composed of a single crystal.\*\* This is done by drawing the tungsten through dies at a certain rate and temperature. The molybdenum wire tested by Sykes was prepared in the following way:—The wire of diameter 0.027 of an inch was equi-axed by heating in hydrogen for 5 seconds at 90 per cent. of its fusion ampèreage. The wire was then at a low red heat drawn through a 0.025-inch die and its cross-section reduced by

\* 'Proceedings of the International Assn. for Testing Materials, 6th Congress,' vol. 2, No. 6 (1912).

† 'Trans. of Amer. Inst. of Mining Engineers,' vol. 47, pp. 569–586 (1913).

‡ 'Journ. of the Iron and Steel Inst.,' 1914, No. 1, pp. 460–496.

§ 'Journ. of the Inst. of Metals,' vol. 20, No. 2, pp. 109–140 (1918).

|| 'Journ. of the Inst. of Metals,' vol. 20, No. 2, pp. 141–145 (1918).

¶ 'Journ. of the Inst. of Metals,' vol. 20, No. 2, pp. 162–165 (1918).

\*\* 'Jahrbuch der Radioakt.,' November 15, 1918, pp. 270–292.

14 per cent. This wire was then heated in hydrogen. Sykes reports that many of the crystals extended completely across the diameter of the wire, and that the average diameter of the crystals was 0.013 of an inch, and the maximum length 0.5 of an inch.

In 1920 the present authors published the results of an extended investigation on "Crystal Growth and Re-crystallisation in Metals,"\* in which were included a number of tests on the production of large crystals in aluminium sheet 0.125 of an inch in thickness, and their conclusions may be summarised as follows:—(1) The largest crystals are always formed at the minimum stress requisite to produce growth, which minimum is determined by the temperature of heating. (2) The lower the temperature of heating the greater the stress required to produce the largest crystals obtainable at that temperature. (3) There is no gradual increase in size from the original sized crystals up to the largest; the latter appear to form directly from them. (4) Test-pieces strained and heated at a low temperature, which nevertheless is sufficient completely to soften the metal—for instance at 350° C.—show no crystal growth at that temperature. Nevertheless, if subsequently heated at a higher temperature, they produce large crystals equal in size to those normally produced at that temperature for the same degree of elongation.

The purity of the aluminium upon which these experiments were carried out did not exceed 98.9 per cent., the principal impurities being silicon and iron. Later experiments showed that crystals of a much larger size could be produced in purer sheet. It was therefore decided to repeat the previous experiments with the purest obtainable metal. This was kindly furnished by the British Aluminium Company, and found to contain 99.6 per cent. of aluminium, the chief impurities being silicon 0.19 and iron 0.14 per cent. In the strain-hardened sheet the silicon appears to be wholly dissolved, but the greater part of the small amount of iron present was segregated as the aluminium-iron compound,  $\text{FeAl}_3$ . The total length of the test-pieces was 8.75 inches, with a parallel portion 4 inches long, 1 inch broad, and 0.125 of an inch thick. The broad ends were  $2.75 \times 1.75 \times 0.125$  of an inch. The test-pieces were in the first instance heated for 6 hours at 550° C., so as to remove all strain-hardness and produce uniform equiaxed crystals. This resulted in a material containing, on an average, 150 crystals to the linear inch. They were then stressed by varying amounts, shown in Table I, so as to produce extensions of 1 per cent., 2 per cent., 3 per cent., etc., on 3 inches until, at a stress of 4.7 tons per square inch, the total extension was 30 per cent. They were next heated for 18 hours at 550° C., and etched. The surface

\* 'Journ. of the Inst. of Metals,' vol. 24, No. 2, pp. 83-131 (1920).

of the sheet was remarkably good, and required no preparatory treatment before etching. The results were similar to those obtained with the less pure sheet, except that the largest crystals were found in the test-piece which had stretched only 1 per cent. whereas in the latter case no growth was obtained under 3 per cent. extension at the same temperature. Moreover, more than half of the specimen, which had stretched only 1 per cent., consisted substantially of one crystal with a few unabsorbed small crystals on the surface. The crystals in those test-pieces which had received an elongation of 2 per cent. and upwards were all correspondingly smaller. Finally, the complete series of test-pieces—18 in all—were broken under tensile stress.

Table I.

Mark.	Percentage elongation given. Calculated on 3 inches.	Load tons per square inch required to produce elongation.	After heating for 18 hours at 550° C.	
			Ultimate stress tons per square inch. Calculated on new area.	Percentage elongation on 3 inches.
2	1	1.6	3.1	23
3	2	2.3	3.4	37
4	3	3.0	3.2	27
5	4	3.3	3.3	35
6	5	3.5	3.9	29
7	6	3.7	3.7	30
8	7	4.0	3.8	23
9	8	3.9	4.1	*22
10	9	4.1	4.3	*24
11	10	4.2	4.6	34
12	11	4.3	4.6	35
13	12	4.3	4.6	35
14	14	4.4	4.6	34
15	16	4.4	4.6	39
16	18	4.6	4.6	36
17	20	4.6	4.5	35
18	25	4.7	4.3	33
19	30	4.7	4.5	30

\* Broke outside gauge marks.

The results of the tensile tests are given in Table I. It will be seen that the ultimate stress is lowest for the largest crystals, and that it increases fairly uniformly up to an initial elongation of 10 per cent., at which point it becomes steady until after an elongation of 20 per cent. when it falls slightly. The figures range from 3.1 to 4.6 tons per square inch. (The average breaking stress for the sheet as delivered, after it has been heated for 6 hours at 550° C., is 4.6 tons per square inch (Table II).) Slight variations in the figures can be ignored, since a uniform rate of loading is not possible in this material owing to large slips which take

place in jerks. The extensions measured over 3 inches are very variable, particularly where the crystals are large. This is evidently due to the fact that in some pieces the crystals elongate more easily than in others, and this has a marked effect when the whole test-piece consists of comparatively few crystals. The low figure obtained for the test-piece, which had had a preliminary extension of 1 per cent., is partly due to the presence of small unabsorbed crystals on the surface.

*Production of Single Crystals in the Sheet.*

The problem which the authors next set themselves was to convert the crystals in the parallel portion of the test-piece, 4 inches  $\times$  1 inch  $\times$  0.125 of an inch, into a single crystal. As already stated, the number of crystals in a linear inch, after treatment for 6 hours at 550° C., was about 150. Calculation, therefore, shows that the total number contained in the parallel portion of the test-piece was about 1,687,000.

Before describing the experiments undertaken with this object, it is necessary to refer very briefly to certain results established by the authors in their paper previously referred to.\* The structural changes produced in a crystal aggregate by deformation followed by heat may be summarised somewhat in the following way:—The first effects are slight. They are revealed by slip bands and in some cases, twins. The former are completely, and the latter to some extent, removed by heating. No change is observed in the shape of the crystals. The boundaries appear unaffected, and, apart from twinning, there is no change in orientation. Thus far, only the interior of the crystals is affected. No identities are lost. Somewhat greater deformation, however, produces crystal growth, and at this stage the boundaries of the crystals become active. The activity is shown in the capacity of the growing crystal to push forward its boundary in certain directions, thus invading other crystals. But, even at this stage, the orientation of the growing crystals is maintained. That of the crystals grown into is, of course, destroyed unless it happens to be the same. The third stage, produced by still greater deformation, appears to take place exclusively in the boundaries of the deformed crystals. It is here that the new crystals are born, indicating the destruction of the original crystals and a complete scheme of orientation. Whereas, therefore, the early effects of deformation are shown only in the interior of the crystals, the later ones appear to take place entirely at the boundaries.

The abnormally large crystals formed on heating, after a small deformation and the gradual decrease in their size as the deformation increases, are

\* 'Journ. of the Inst. of Metals,' vol. 24, No. 2, pp. 83–131 (1920).

considered by the authors to be due to the following causes:—As already mentioned, the first effect of small amounts of deformation is to produce slip bands (and in some metals twins), but, provided the stress does not exceed a certain value, this is all that happens. A very little more deformation, however, causes a change in a few of the crystals, so that, on heating, they grow. The less the strain the fewer the centres from which growth will start, and hence the larger the crystals ultimately formed. In the case of the impure aluminium sheet, the largest crystals began to appear after 2 per cent. elongation, followed by heating at  $550^{\circ}\text{C}$ . But their capacity for growth was exhausted when only about half of the total number of crystals had been absorbed. At  $645^{\circ}$ , however, they were able to effect complete absorption, owing to the greater mobility conferred by the higher temperature. But the higher temperature enabled the growth to start from more centres, so that the final crystal size was smaller than at  $550^{\circ}$ . Similarly, as the deformation increases, more crystals will be strained to the critical amount to produce growth on heating, and there will accordingly be a corresponding decrease of crystal size. In a given case, where 2 per cent. elongation, followed by heat treatment at  $500^{\circ}$ , produced no growth, whereas 4 per cent. gave rise to the largest crystals, about ten crystals in all out of the many thousands present were strained in the critical amount, which enabled them to absorb all their neighbours on heating. It is, of course, possible to imagine a case in which only one of these crystals was strained to the critical amount which would have had to have been rather less. In this case it would be expected that the whole of the strained area would ultimately have consisted of one crystal instead of ten, provided that suitable conditions were maintained. One condition, which the authors regard as essential, is that all the remaining crystals must also be in a strained condition. As bearing on this, it should be pointed out that there was nearly always a strip of small unaltered crystals on either side of the flat ends of the test-pieces, even when they had been heated at  $645^{\circ}\text{C}$ , and that the large crystals showed no tendency to grow into them. Owing to their position, they had not been strained by the pulling of the test-piece. It seemed clear, therefore, that the crystals must all be strained to some extent if they are ultimately to be absorbed by one. The high temperature, if not absolutely necessary, is certainly a favouring condition, since it confers increased freedom of movement on the crystals, but the actual temperature at which growth progresses most favourably depends on the degree of deformation. The conditions laid down by the authors in their previous paper (p. 122) for the production of a single crystal were therefore "that every crystal in the complex shall be strained a certain small amount, and

that one of them shall be strained rather more than all the rest." They went on to say "how unlikely it is that such a condition would ever be realised in practice it is unnecessary to emphasise, but, theoretically, such a case can quite well be conceived." This prognostication has not proved to be correct, and, before many months had passed, the authors had succeeded not only in converting all the crystals in the parallel portion of one test-piece into a single crystal, but had worked out conditions under which fully 25 per cent. of the test-pieces thus treated were converted into a single crystal. With regard to the remainder, some of them consisted of two, others of three, and others of four crystals, but it was very seldom that the last-named figure was exceeded.

To achieve these results, the high purity metal (99.6 per cent.), with which all subsequent experiments have been conducted, was subjected to three treatments, two of them thermal, the third mechanical. As received, the sheet was in the cold-rolled condition. It had first to be heated, so that it might be softened and re-crystallised. It had next to be strained to the required amount, and finally it required to be heated so that the potentiality of growth conferred by the stress could be brought fully into operation.

1. *The Temperature and Time of Heating before Stressing.*—The most suitable temperature was found to be 550° C. and the time 6 hours. If heating was continued for longer, large crystals formed on the surface of the sheet in many cases, and the test-pieces were rendered useless, because the stress subsequently applied produced a greater elongation, which was localised to a large extent in these crystals, and consequently the strain was not uniform. If heated at a lower temperature, the crystals finally produced on heating for a given load and elongation were smaller, but the results were very variable. The same result followed at 550° C. if heating was continued for a shorter period, for instance, 2 hours. In all such cases the results were very variable, but they tended to show that the largest crystals were more frequently formed when the temperature had been high and maintained for a sufficient period to produce stable conditions in the metal.

2. *The Stress applied and Percentage Elongation caused.*—In previous experiments the method adopted had been to stretch the test pieces in tension by a given amount measured by means of dividers on 3-inch gauge-marks. This method was not capable of very accurate adjustment and was discarded in favour of pulling with a given load and then measuring the extension. The advantage of this method was that the stress was always constant and the variations in elongation were very slight. Moreover, a large number of test pieces could be stretched with ease and rapidity. The procedure finally adopted was to pull to some definite fraction of a ton per square

inch, which would give approximately the required elongation. A load of 0.20 of a ton, *i.e.*, 1.6 tons per square inch, gave an elongation of 0.8 per cent. on 3 inches. If such a test-piece was subsequently heated, large crystals were produced, but small surface crystals frequently remained unabsorbed even after many hours' heating at 550° to 600°. A load of 0.30 of a ton finally proved the most suitable. This is equivalent to 2.4 tons per square inch and gave an average elongation of 1.6 per cent. on 3 inches.

3. *The Temperature of Heating after the Application of Stress.*—It was found that large crystals began to form usually at about 500° C., or even under in some specimens, but not until 520° C. in others, although the treatment had been identical in the two cases. It was also found that the lowest possible temperature at which growth took place at all was the most suitable for growing the largest crystals. Consequently, each test-piece was placed in a furnace whose initial temperature was 450° C. and the temperature raised at from 15° to 20° C. per day up to 550° C. It was then subsequently heated for 1 hour at 600° C. in order to complete the absorption of small crystals on the surface, which persistently remained at lower temperatures. This method proved, on the whole, to be the best; but even so, on an average not more than one test-piece in four is converted into a single crystal over the parallel portion of the test-piece. The time required for a single crystal to form from the 1,687,000 can only be stated approximately, for it has been found to vary within tolerably wide limits, and, as just mentioned, some of the small surface crystals only disappear after fairly prolonged heating, but in the majority of cases the result can be achieved in from 48 to 72 hours. A test piece is, of course, much more quickly converted into three or four large crystals than into one, since in the former case growth takes place simultaneously from several centres. In such cases, when the large crystals have set, the authors have not found that they grow at each other's expense, even if the temperature be raised or the time of heating extended. In this respect they resemble the crystals of castings which also grow from various centres until they meet and are then stable.

Certain variations of the above methods were subsequently tried, but none of them were found to give greater regularity of results, although some of them established facts which bear on the question of how single crystals are actually produced. Prolonged heating at a low temperature, or starting the heating from a low temperature, for instance 250°, and gradually raising it, was not found to affect the crystal size. It was established that if the test pieces were more severely stressed, the temperature at which the maximum crystal size was produced was lowered. It was, therefore, to be expected that, provided the temperature at which heating was commenced was

sufficiently low, all the test pieces within certain limits of stress should give the same sized crystals on heating. A series of test-pieces was stretched 1, 2, 3, 4, and 5 per cent., heated at 250° C., and the temperature then gradually raised to 550°. In the pieces stretched from 1 to 4 per cent. the number of large crystals produced was approximately the same, although certain differences were manifest. In that stretched 5 per cent., however, the crystals were much smaller, indicating that, however much the temperature may be lowered, there is an upper limit to the stress which will produce the largest crystals.

If the optimum conditions for the production of a single crystal throughout the parallel portion of the test-piece are maintained, as previously described, on an average one experiment in four is successful. There are, however, considerable variations from batch to batch. For example, in a given case eighteen test-pieces, which had received, as nearly as possible, the same heat and mechanical treatment, gave the following results, which must be understood to refer only to the parallel portion of the test-piece,  $\frac{1}{4}$  inches  $\times$  1 inch  $\times$  0.125 of an inch:—Two test-pieces consisted of one crystal, six of two crystals, five of three crystals, three of four crystals, and two of six crystals. In another batch, out of twenty test-pieces, seven consisted of one crystal, eight of two crystals, four of three crystals, and one of four crystals. The best result hitherto achieved has been in a batch where nearly half the test pieces were converted into a single crystal over the length in question.

#### *Tensile Strength Tests.*

When composed of small crystals as obtained by heating for 6 hours at 550° C. the sheet gives uniform results on breaking. A few examples are given in Table VII, p. 342, from which it will be seen that the ultimate stress varies from 4.5 to 4.7 tons per square inch, and the percentage extension on 3 inches from 36 to 38. The sheet necks slightly at the fracture, which is usually straight. This is the standard of comparison from which the behaviour of single crystals may be judged. Its condition is described by the authors as "normal" and photograph is given in Plate 10, fig. 12. The roughening of the surface due to the large number of small crystals is evident.

The values obtained in tests of specimens consisting of single crystals varied from 2.80 to 4.08 tons per square inch, while the extension varied from 34 to 86 per cent. measured on 3 inches. These variations in properties were accompanied by differences in the method of stretching and type of fracture, and these differences have provided a means of classifying the test-pieces. In certain cases the mechanical properties, especially the extension, were found to be closely related to these characteristics. The test-pieces have been



classified in the following five groups. Not all of them showed the various features to the same extent and some were almost on the border line between two groups:—

*Type 1.*—The test-pieces narrowed in breadth gradually from the shoulders towards the fracture. The reduction in breadth near the fracture was often great, *i.e.*, the metal necked sometimes almost to a point (Plate 9, fig. 2). The sides (machined edges of the sheet) remained perpendicular and the reduction in thickness was only from 2 to 3 per cent. Slip bands were usually absent from the surface, but large slips were frequent near the fracture, forming steps on the sides and smaller markings on the face.

It was noticed in some specimens that a large slip occurred over one half and this then held while a similar slip took place on the other half. The process was then repeated until the test-piece broke (fig. 3, and Diagram I). Slip in this case took place in the direction of pulling and at right angles to the



DIAGRAM I.

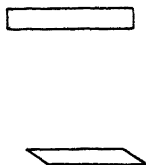


DIAGRAM II.

plane of the sheet. With a view to following the distortion of the specimens during the test some of them were ruled in squares (0.25 inch) by means of a fine needle point. The results showed that the squares became diamond-shaped, that they had both narrowed and elongated and at the fracture the lines at right angles to the axis were frequently bent at an angle of 45°. Figs. 1 and 2, Plate 9, are examples of this type and fig. 16, Plate 10, shows the change in shape of the squares. The results of seven tensile tests will be found in Table II, from which it will be seen the extreme values for the tenacity were 2.9 and 3.9 tons per square inch and those of the elongation 57 and 67 per cent.

*Type 2.*—In this case the test piece remained broad, losing sometimes only 1 per cent. in breadth, but became very thin with a uniform reduction of thickness of about 45 per cent. The sides tended to slope slightly in the same direction away from the perpendicular. Slip bands on the surface were well marked and their main direction was across the test-piece, that is, at

right angles to the axis. There was no necking at the fracture, the test-piece remained broad but drew down to a knife edge and then parted in a straight line, either at right angles to the axis or inclined at some other angle to it. If the test-pieces were marked in 0.25 or 0.50 inch squares before being pulled the lines at right angles to the axis did not become inclined to the same extent as in specimens of Type 1. They merely drew further apart, while the position of the lines parallel to the axis did not alter. Although the squares were only lightly scratched on the surface with a needle point, the cross lines affected the internal structure to such an extent that they were revealed on the opposite side of the test-piece by means of interruptions in the slip bands (fig. 3, Plate 9). This phenomenon was only met with in specimens of this type and is no doubt due to the particular direction of the slip bands in relation to the stress. This type, therefore, shows slipping in the plane of the test-piece in the direction of the stress (figs. 3 and 4, Plate 9). Fig. 13, Plate 10, shows test-pieces which had been marked in 0.25-inch squares before being pulled. Values obtained in the tests will be found in Table III. from which it will be seen that the ultimate stress varied from 2.8 to 3.3 tons per square inch and the extension from 47 to 73 per cent.

*Type 3.*—In these cases the test-piece both narrowed and thinned uniformly. There was no necking at the fracture, which went straight across the test-piece, as in Type 2, either at right angles to the axis or inclined at some other angle. A notable feature of this type is the sloping of the sides, so that a section after pulling is no longer a right angle but a parallelogram with alternate acute and obtuse angles. The side-ways slipping, which caused the test-piece to take this form, was entirely absent from Type 1, and only occasionally slightly evident in Type 2. It always occurs in this group, although not always to the same extent. Slip bands were usually well worked, and were inclined to the axis at different angles. Squares marked on the specimens by a needle-point both narrowed and elongated, and became diamond-shaped owing to the lines at right angles to the axis inclining towards it. Although similar in that respect to Type 1, they differed in that the diamonds were more uniform in size and shape over the whole test-piece. In other words, the elongation was more general and uniform. This type, in contra-distinction to the two previous ones, shows slipping in two main directions. It elongates in the direction of the stress by slips nearly parallel with the plane of the sheet, and also at right angles to the plane of the sheet but parallel with the axis. Inasmuch as these planes are not at right angles to the direction of the stress, there is also a sideways slip as the crystal endeavours to accommodate itself to it, and this accounts for the change in shape of the cross-section of the test-

piece. Table IV gives the results of fifteen different tests in which the extreme values for the ultimate stress are 2.9 and 4.08 tons per square inch while the extension over 3 inches varies from 34 to no less than 86 per cent. There are greater variations in tensile properties in this group than in any other. Examples will be found in figs. 5, 6 and 7, Plate 9.

*Type 4.*—This unites the qualities both of Type 1 and Type 3, in that the test-pieces not only narrowed and thinned, but in addition, necked at the fracture. In all cases a sideways slip was evident. The actual values obtained in the tests will be found in Table V. With one exception, the ultimate stress values are very similar, while the extensions were in all cases high, partly owing, no doubt, to the necking at the fracture. An example of this type is seen in fig. 8, Plate 9, while figs. 14 and 15, Plate 10, show the distortion of the 0.25-inch squares as a result of the stress.

*Type 5.*—In this are included all the test-pieces which produced twins on being pulled. No signs of these were visible before stress was applied. In some cases only a few resulted; in others the test-piece was twinned all over. In every case the test-piece buckled and crumpled to a certain extent owing to the shifting of portions of the sheet into the twinning position. The slip bands change in direction as they cross the twin boundary, and where the specimen had been marked in squares these also change direction sharply at the twin boundaries. On heating, re-crystallisation began at these boundaries (fig. 17, Plate 11), although a section cut through this failed, under vertical illumination, to show the well-defined line associated with crystal boundaries. Under oblique illumination, however, the change of orientation is quite evident. Two types of twins were met with. The first resembled the twins produced in tin and zinc, although, owing to the large size of the crystals, they were on a much larger scale. They appeared like large fibres. A fracture across them was uneven, and the thickness of the sheet at the fracture differed from twin to twin. Examples are given in figs. 9 and 10, Plate 10. The second type of twinning observed was one in which the twinning planes were almost straight. Such a twin is shown at the top of the test-piece indicated in fig. 11, Plate 10. It appears as a narrow, dark line starting just at the shoulder of the test-piece, and running up into the broad end. Twins of this type also formed frequently on each edge of the test-piece. In a given case, on one side the entire edge turned up, while the edge on the opposite side turned down. Figs. 18 and 19 show a part of the surface in which, in addition to twinning on the edge, a twin has also been formed at the centre. A section of this crystal (fig. 19) shows how the twins at the edges turn in opposite directions, and also the step up at the twin in the centre. It will also be noticed that the twinning

planes across the crystal are all parallel. As in the previous case, under vertical illumination, no line marks the boundary between the twins, but they are rendered perfectly clear by oblique illumination. This type of twinning is similar to that produced by the well-known method of causing twinning in calcite. By pressing a knife on the acute angle of a calcite rhomb near the edge, a portion of the crystal can be bent right over, making a definite angle with the unaltered face. This experiment was first performed by Baumhauer. The test-pieces which showed twinning were usually broad and thin, resembling Type 2. Twins were sometimes found amongst specimens of the other types, particularly near the boundary of an intruding crystal as, *eg.*, in the lower half of fig. 11, Plate 10. Numerical values of the tests of this type will be found in Table VI. The figures of the percentage extension are the most uniform of the five types.

Table II.

Type.	Test-piece number.	Tensile strength. Tons per sq. in.	Elongation per cent. on 3 inches.
I. Test-pieces necked, thick, straight sides. Slip bands usually absent on surface.	22	3·1	66
	83	3·3	59
	98	3·5	57
	125	3·9	58
	130	2·9	65
	134	3·7	63
	210	3·1	67

Table III.

Type.	Test-piece number.	Tensile strength. Tons per sq. in.	Elongation per cent. on 3 inches.
II. Test - pieces broad and thin, straight fracture, slightly sloping sides. Slip bands nearly at right angles to axis of test-piece.	102	2·9	52
	172	3·1	65
	186	3·1	47
	198	3·3	67
	204	2·9	66
	264	3·1	74
	285	2·8	73

Table IV.

Type.	Test-piece number.	Tensile strength. Tons per sq. in.	Elongation per cent. on 3 inches.
III. Test-pieces narrow and thin, straight fracture, sloping sides. Slip bands sloping in relation to axis.	68	3.2	64
	74	3.3	48
	84	3.1	75
	114	3.1	58
	118	3.0	74
	119	3.3	55
	135	3.4	53
	191	3.1	60
	197	3.1	59
	207	3.1	74
	218	3.1	44
	252	3.8	34
	256	2.9	86
	261	3.1	76
	269	4.08	64

Table V.

Type.	Test-piece number.	Tensile strength. Tons per sq. in.	Elongation per cent. on 3 inches.
IV. Test-pieces narrow and thin, straight fracture necked, sloping sides. Slip bands sloping in relation to axis of test-piece.	96	3.2	66
	132	3.8	62
	184	3.1	75
	189	3.1	60
	194	3.1	76
	214	3.1	79
	220	3.3	53
	263	3.2	75

Table VI.

Type.	Test-piece number.	Tensile strength. Tons per sq. in.	Elongation per cent. on 3 inches.
V. Crystals twinned; other features variable.	82	3.4	55
	86	3.0	67
	116	3.0	56
	213	3.8	57
	270	3.0	55

Table VII.

Condition.	Test-piece number.	Tensile strength. Tons per sq. in.	Elongation per cent. on 3 inches.
Sheet as received, heated 6 hours at 550° C. About 150 crystals to the linear inch.	111	4.5	38
	289	4.7	37
	290	4.7	37
	291	4.6	37
	292	4.5	36

*Stress Tests of Test-Pieces consisting of two Crystals.*

Each crystal in a test-piece consisting of two or more crystals behaves according to one of the five types described above, provided that the whole test-piece at the point of fracture consists of a single crystal. A considerable number of specimens composed of two crystals were fractured in tension and almost every combination of the five types was met with. In the majority of cases tested the crystals occurred end to end in the test-piece and fracture always took place across one or other of the crystals, but never at a boundary. The influence of one crystal in giving support to the other at the boundary was most marked. Its effect was often noticeable at a distance of 0.25 inch from the boundary. Reduction, both in thickness and breadth was much less at this point and the power to withstand deformation was considerably increased, especially where one crystal slipped to the left and the other to the right. The metal drew down on either side of the boundary and left it as a ridge sometimes pronounced in thickness, at other times in breadth. In many cases the sheet looked as if it had been twisted in testing. It is not difficult, however, to account for these irregularities when it is remembered in what different ways the single crystals extended in tension. A crystal which narrowed on pulling in contact with one which remained broad tended to make the latter narrow also, with the result that it frequently wrinkled and twinned, in the vicinity of the boundary. In its turn, the crystal which remained broad, tended to prevent the other one from narrowing and this produced a thickening of the latter. Figures of some of these test-pieces show the effects referred to above. In fig. 20, Plate 11, will be observed three test-pieces in which the distortion at the junction of the two crystals is very manifest. Fig. 21, Plate 12, gives an edge-wise view of five fractured test-pieces in which in each case the combination of types there included is mentioned. This shows very clearly the different extents to which the crystals have been distorted and the influence of the junction.

In cases where two crystals existed side by side in the test-piece fracture occurred across them and one crystal frequently broke before the other. In this case the latter crystal continued to elongate until it also broke, with the result that when the test-piece was subsequently put together there was sometimes a gap of 0.25 inch between the fractured halves of the first crystal. A list of tests carried out on 18 test-pieces consisting of two crystals is given in Table VIII. As in the case of single crystals the values both for tenacity and extension are very variable. The elongation values are, for the most part, somewhat lower but the total elongation gives no indication of the amount of stretch on each individual crystal. When the test-piece was

marked in 0.25 or 0.5 inch squares before pulling, it was possible to measure the elongation on 1 inch in each crystal and the figures so obtained have been included in a few cases. These are not strictly comparable as one of them includes the fracture. In the following examples, however, fracture occurred outside the gauge marks and the figures represent the actual elongation of each crystal under the same load:—

Total elongation on 3 in.  
49 per cent.

Crystal No. 1 on 1 in.  
71 per cent.

Crystal No. 2 on 1 in.  
25 per cent.

The crystals in each case are classified according to the five types previously described. The great majority of combinations are represented in this list.

Table VIII.—Test-pieces consisting of Two Crystals.

Mark.	Tensile strength. Tons per sq. in.	Percentage elongation on 3 inches.	Type of crystals.		Percentage elongation on each crystal on 1 inch.	
			Fractured.	Other.	Fractured.	Other.
42	3.2	32	Type I	Type III		
75	3.2	54	" IV	" III		
81	3.5	29	" III	" III		
87	3.1	55	" IV	" III	61	52
122	3.0	46	" V	" I		
123	3.0	38	" II	" II	67	29
126	3.2	51	" III	not altered		
129	2.9	68	" II	Type III		
138	3.0	49	" II	" III		
145	2.9	66	" III	" III		
156	2.8	48	" V	" III		
251	2.9	42	" III	" III		
253	3.1	70	" IV	" IV		
265	3.1	63	" V	" II	71	63
271	3.2	50	" I	" II	86	29
279	3.1	51	" II	" II	81	17
280	3.5	55	" II	" III	94	17
281	3.0	48	" III	" V		

*Test-pieces consisting of Three Crystals.*

The results very much resemble those obtained with the test-pieces consisting of two crystals. The type of crystal which fractured could be judged without difficulty, but it was sometimes quite impossible to identify the others, especially if they did not undergo much deformation when fracture occurred. A few examples are given in Table IX. In all of these, each crystal extended over the entire cross-section of the test-piece. They were joined end to end. Here also fracture always occurred across a single crystal.

Table IX.—Test-pieces consisting of Three Crystals.

Mark.	Tensile strength. Tons per sq. in.	Percentage elongation on 3 ins.	Type of crystal.		
			Fracture 1.	Fracture 2.	Fracture 3.
127	3.5	36	Type III	Type III	Type III
144	2.9	55	" V	" V	" II
154	3.1	39	" V	" II	" II
272	3.1	53	" IV	" II	" I
278	3.0	54	" I	Not much altered: doubtful	Not much altered: doubtful.
284	3.1	44	" II	Type I	Not much altered: doubtful.
287	3.6	37	" III	" III	Type I (probably).

The malleability of the single crystals was very remarkable. In a given case, a crystal was rolled down from the original thickness, 0.125 of an inch. At a certain stage, when it had elongated considerably, it was cut in half, and one of these pieces was rolled down to 0.0094 of an inch, corresponding to a reduction in thickness of 93 per cent. This rolling was done without any annealing, the strip was still quite malleable, and the operation could have been continued further had the rolls permitted it. This malleability is far in excess of that of the sheet, consisting of 150 crystals to the linear inch.

#### *Production of Single Crystals in Bars.*

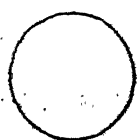
Experiments were next carried out with a view to converting the crystals in a bar of the metal into a single crystal. One inch diameter bars of the same purity as the sheet were obtained by the kindness of the British Aluminium Company. Two sets of test-pieces were machined from them, the diameters being 0.564 and 0.798 of an inch respectively, with a parallel portion of 3.5 and 3.0 inches respectively. These were heated at 550° C. for 6 hours, and given an extension of 2 per cent. on 3 inches and heat treatment, as in the previous tests. On one occasion, out of eighteen test-pieces, eight consisted entirely of a single crystal, and, in three others, one or more small crystals intruded at the shoulders only. The mechanical properties were found to vary in much the same way as in the sheet, and the actual results will be found in Table X. No. 7.7, which has an elongation of 87 per cent. without fracture, being complete, is comparable with the highest elongation obtained with sheet, viz., 86 per cent. The specimens marked with a star were removed from the machine at different stages before fracture was complete, so as to study method of fracture. The elongations are therefore lower than they would have been if the two halves had actually parted.



Table X.—Mechanical Properties of Bar 0·564 of an inch in diameter.

Mark.	Tensile strength. Tons per sq. in.	Percentage elongation on 3 ins.	Number of crystals in bar.
3·10	3·4	76	One crystal.
3·29	3·0	76	" small one at shoulder.
3·30	3·0	78	" which twinned on pulling.
3·31	3·1	68	" small crystals at each shoulder.
3·37	4·0	71	"
10·30*	3·3	56	"
10·31*	3·5	60	" small one at shoulder.
10·33	3·9	55	" two small ones one end.
7·5*	3·8	65	" small one at shoulder.
7·7*	3·06	87	"
3·32	3·4	59	Two parallel crystals, fracture across two.
3·33	3·7	40	Two small parallel crystals at one end: the rest consisted of one crystal in which fracture occurred.
3·35	3·4	66	Three crystals, fracture in one.
3·36	3·1	64	Two parallel crystals at one end; the remainder consisted of one crystal in which fracture occurred.
3·39	3·3	69	Two crystals, fracture across one.
3·41	3·1	77	"
3·42	3·5	50	One crystal at each end and one in the middle across which fracture occurred.
7·8	3·3	50	Two crystals, fracture across one.
10·1	4·82	44	Bar consisting of small crystals.
10·2	4·88	44	Heated for 6 hours at 550° C.

Except that some of the crystals twinned on pulling, there were no different types of fracture such as were found in the sheet. Where a crystal occupied the entire cross-section, the test-piece, flattened in one dimension sometimes as much as 45 per cent., whereas the other dimension differed but little from the original diameter of the bar.

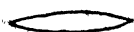


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Diagram III shows (1) a section of the original bar; (2) a section after pulling; and (3) a section at the fracture.



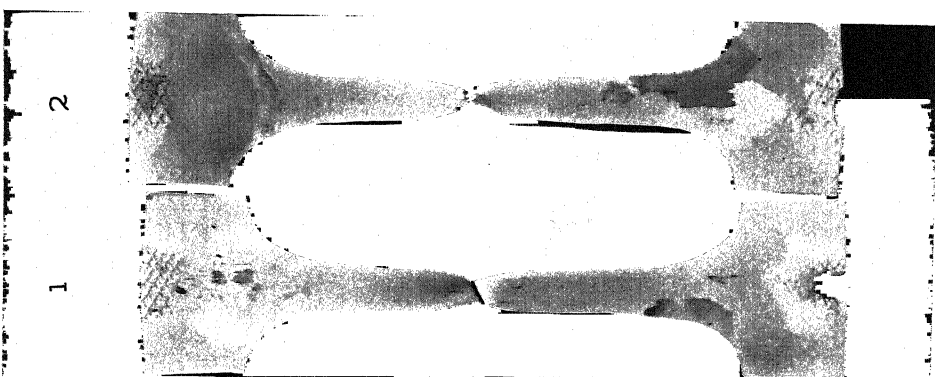
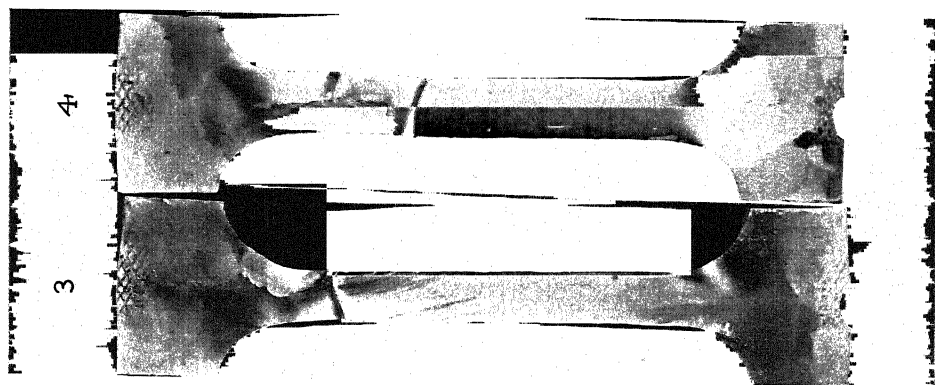
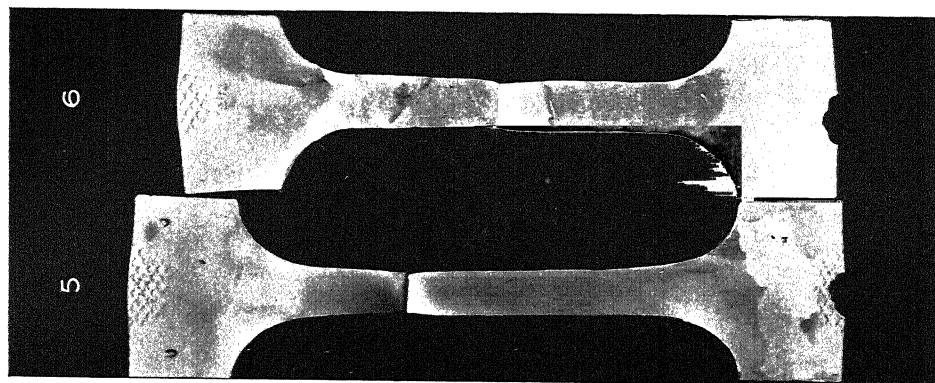
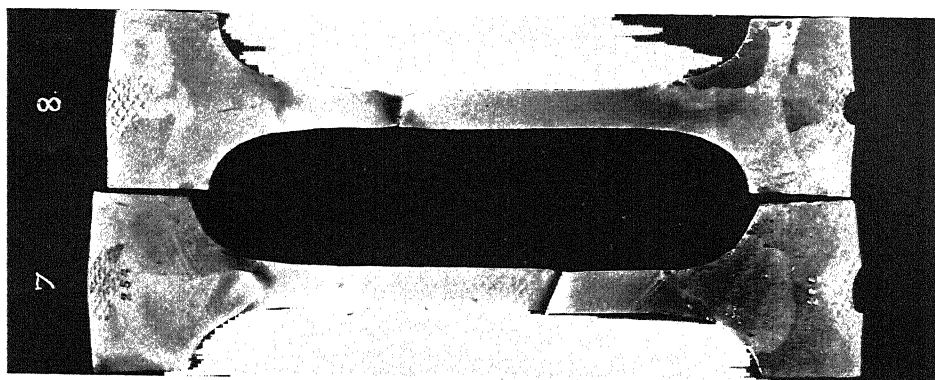
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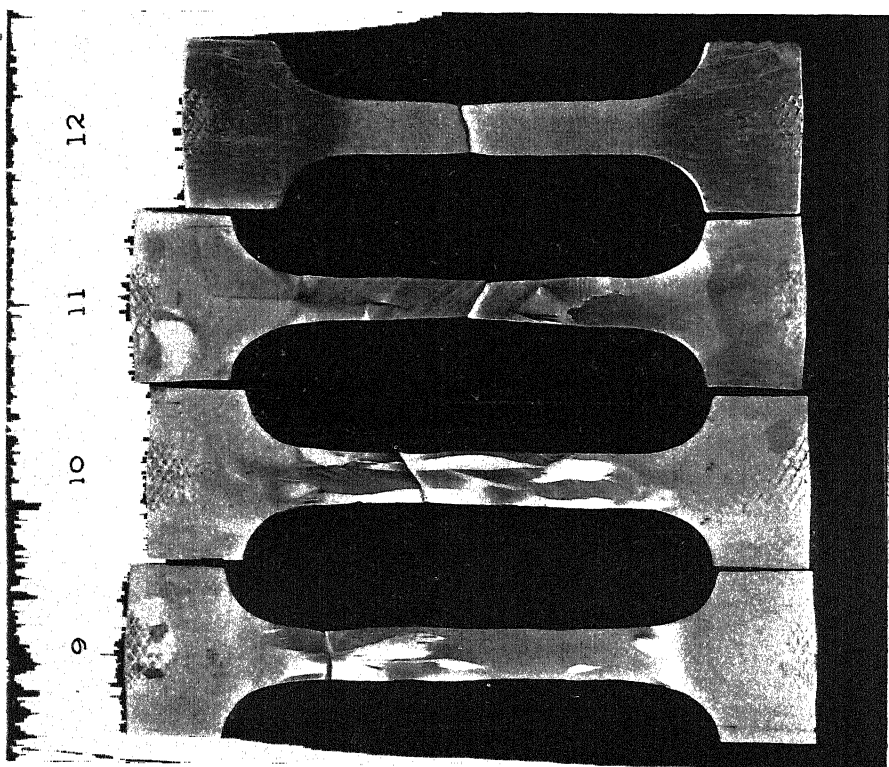
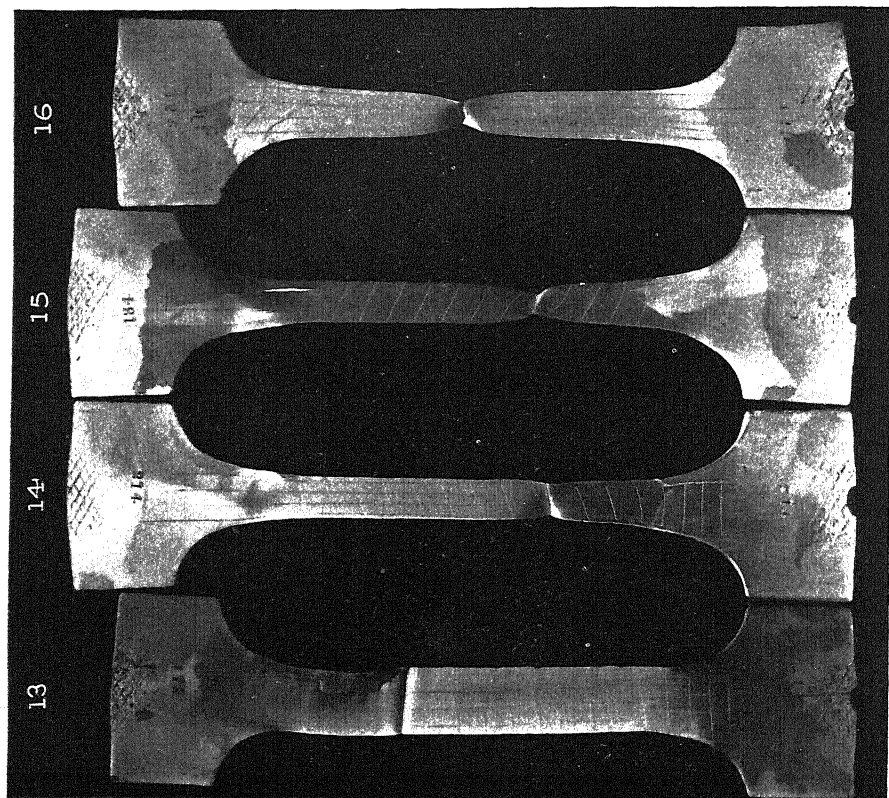


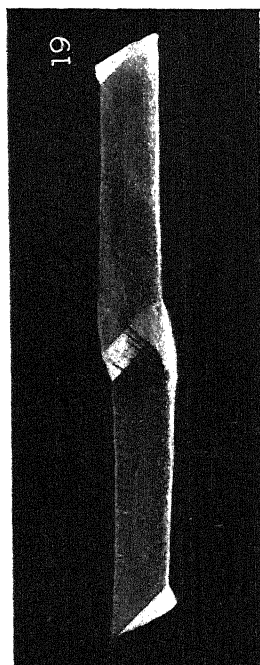
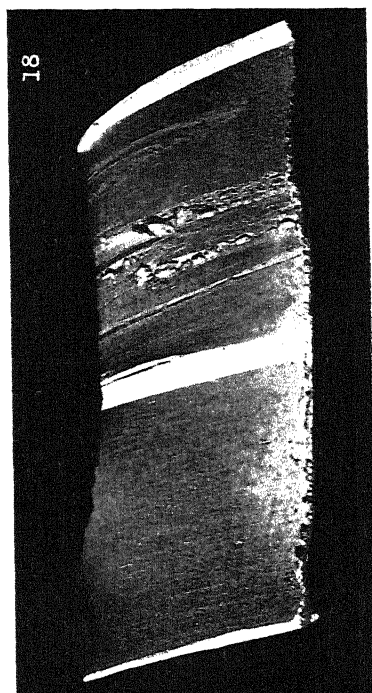
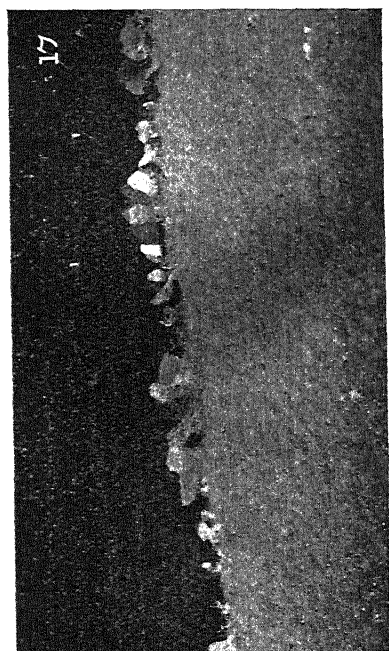
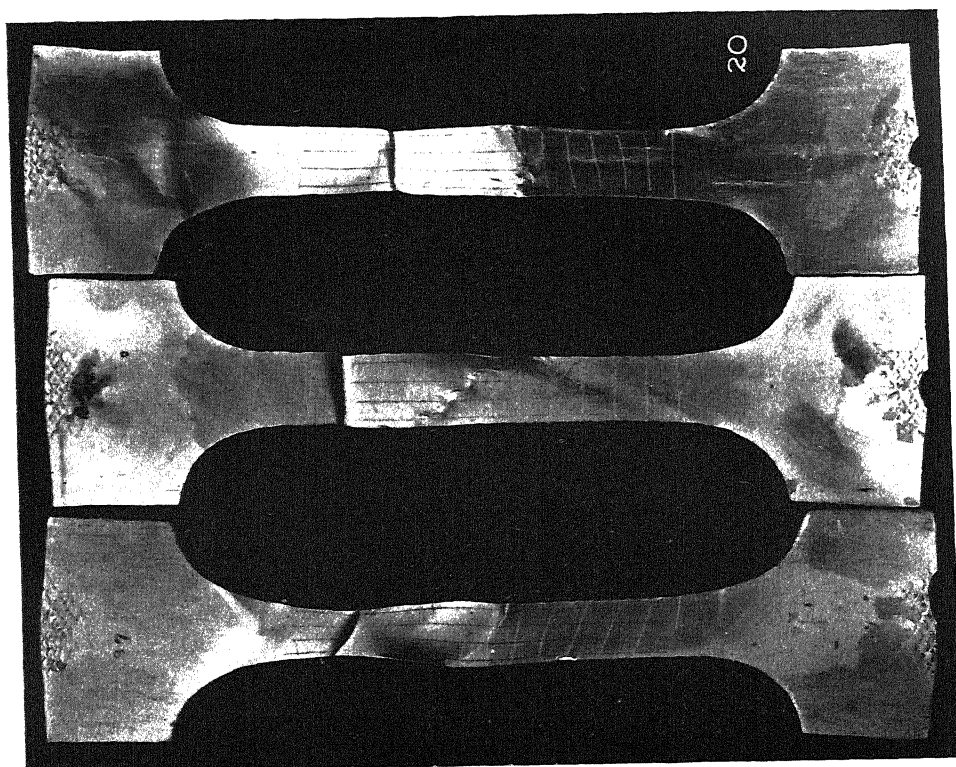
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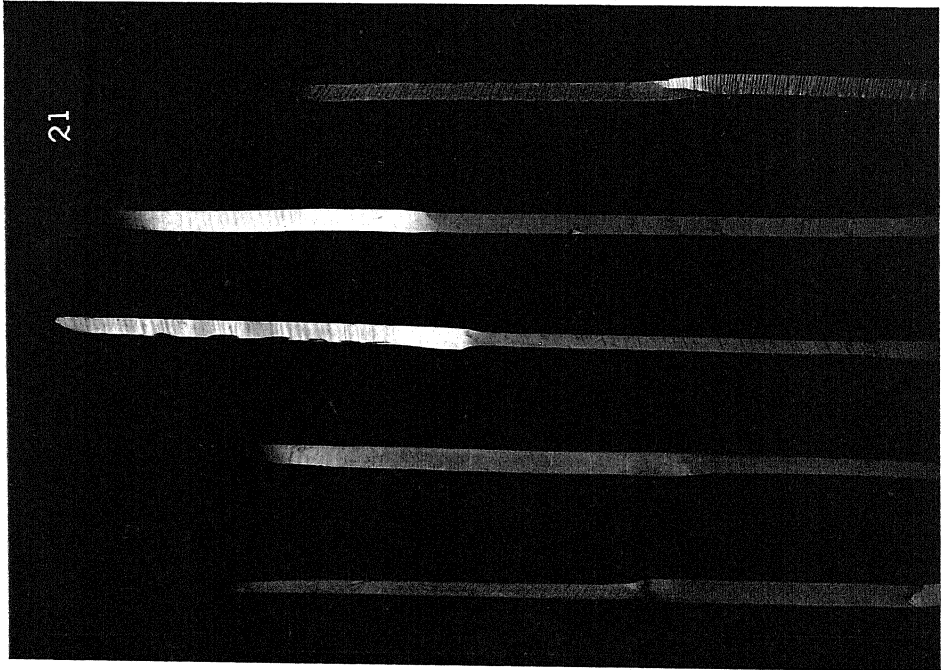
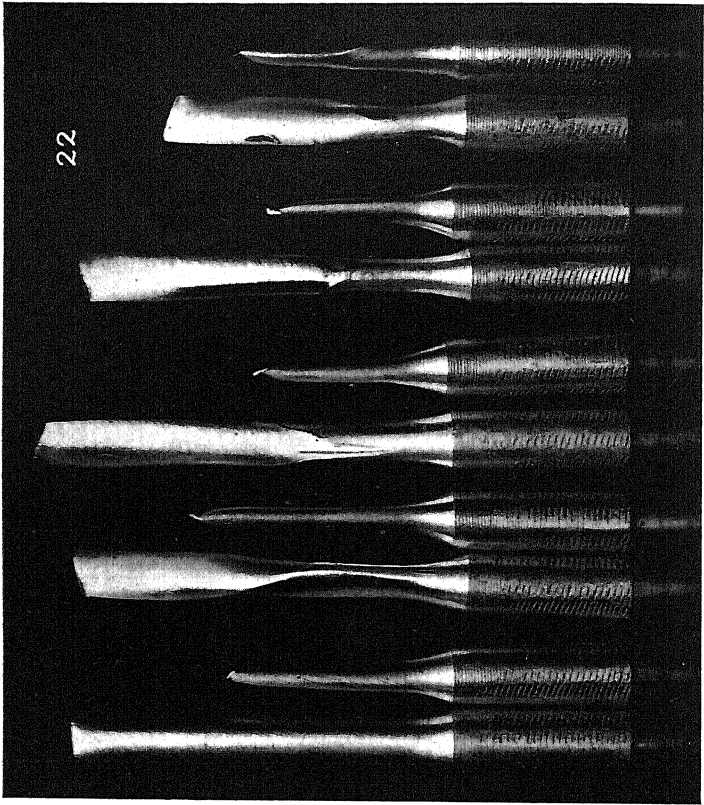
DIAGRAM III.

The method of fracture was peculiar, and can best be described with the aid of diagrams. When the bar began to break, it drew down sharply in the same direction in which it had thinned, and a lens-shaped area was formed (Diagram IV, fig. 1). As the bar pulled apart, this became smaller and smaller (fig. 2). It parted first on both sides, and then in the middle (fig. 3). A section cut through the fracture illustrates the thinning at right angles to the plane, depicted in figs. 1, 2, and 3, and shows the curious grooved fracture with flow lines (dotted, fig. 4), which was always obtained. This type of fracture was found in all the bars where fracture actually











occurred across single crystals. It is quite unlike that of a similar test-piece composed of small crystals, where the section of the bar remains round and

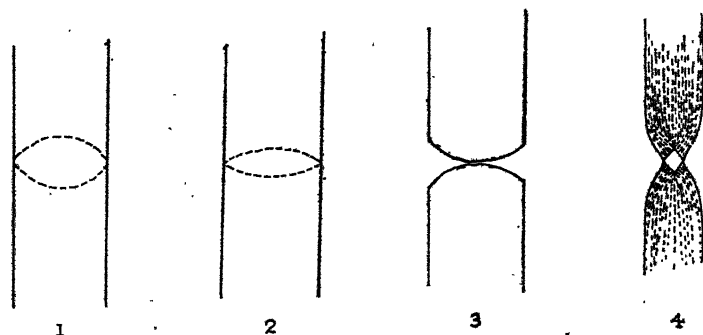


DIAGRAM IV.

necks uniformly. Photographs of some of these bars are given on Plate 12, fig. 22. In each case one half of the test-piece is placed so as to show the broad side, while the other half is turned at right angles to show how the test-piece has thinned. Nos. 30 and 37 were single crystals, the latter twinned on pulling: the remaining three consisted of two crystals. It will be observed in Table X that the tensile strength of the single crystals varied from 3.0 to 4.0 tons per square inch, whereas that of the bar, composed of 150 crystals to the linear inch, was 4.85 tons. The malleability of the single crystals is markedly higher than that of the bar consisting of small crystals.

Considerably more difficulty was experienced in converting the crystals in the 0.798 of an inch diameter bar into a single crystal. After several attempts, however, bars were obtained in which single crystals extended over the entire cross section. In one case the whole of the parallel portion of the test-piece was found to consist of one crystal, while in several others more than three-quarters was thus occupied. Many of the bars consisted of two crystals, but in the majority of cases these existed side by side and not end to end, so that fracture always occurred across both of them. The majority of these bars twinned on pulling, so that the fracture was often uneven and did not show the definite shape obtained in the 0.564-diameter bars. The tensile properties of several bars of this diameter will be found in Table XI.

Some of the original bars, 1 inch in diameter, and some of which only sufficient was removed to reduce the diameter to 0.9 of an inch, were reduced in the same way, but in no case was a crystal obtained extending over the whole diameter of the bar. A cross section usually showed three crystals, but occasionally there were two. Some of the crystals, however, grew to a length of 7 or 8 inches. In addition to round bars, 1-inch square bars were

Table XI.—Mechanical Properties of Bar 0·798 of an inch in diameter.

Mark.	Tensile strength. Tons per sq. in.	Percentage elongation on 3 ins.	Number of crystals in bar.
2·3	4·1	53	Two crystals almost parallel.
2·9	3·9	66	One crystal down one side, two on the other.
2·11	3·8	71	One crystal all down one side, three on the other.
10·17	4·0	42	One crystal extending over the whole section across which fracture occurred. Two crystals at the other end.
10·20	3·8	51	Two crystals, both extending over the whole section. Fracture occurred across one.
10·24	4·1	47	One crystal and two small ones—one at side, one at end.
10·25	4·0	53	One single crystal and a small crystal in one shoulder.

treated. Owing to the shape, these failed to strain uniformly, and on heating, crystals grew from the four corners and met in a line in the middle of the four sides. Some of the crystals were from 2 to 3 inches long and were visible on two adjacent sides. Remarkable effects were obtained on breaking such bars. In some places the corners became rounded, while in others they were narrowed to a ridge almost of a knife-edge thinness. The whole bar became very much twisted and distorted. An attempt was made to measure the Brinell hardness number on two adjacent sides of the same crystal. The lowest available load was 500 kgrm. and the depression made was so large, owing to the softness of the metal, that it could not be made on one side without affecting the other. It was, however, possible to make depressions in some crystals which were sufficiently near the centre of the bar to obviate all risk of being affected by the edges. These were not round, as is the case with metal consisting of small crystals. Most of them were almost square with rounded corners, but they differed from crystal to crystal according to

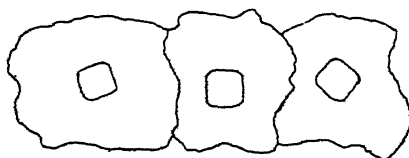


DIAGRAM V.

the orientation. Depressions made at a crystal boundary were very distorted. Diagram No. 5 shows Brinell depressions produced in three crystals.

The effect of heat on the broken test-pieces was to bring about recrystallisation, *i.e.*, the birth of new differently oriented crystals. The temperature at which this began and the size of the new crystals produced depended on the amount of deformation of each particular crystal. The crystals which had

been least deformed produced the largest new crystals. It was always found that the new crystals grew from the region of maximum stress, *e.g.*, from the fracture itself, from scratches on the surface, and from crystal or twin boundaries. On heating a broken single crystal the smallest of the new crystals are found at the fracture, and the size increases up to the shoulders, where the stress has been least. The new crystals were elongated in the direction of pulling, but frequently sloped sideways, as if following the direction of the slip bands. Some of the new crystals showed well-marked twins, resembling those in copper and brass, and one example was obtained in which the twinned crystal completely penetrated the sheet.

In the preceding pages, a description has been given of the methods whereby single crystals of aluminium have been produced, and their behaviour under tensile stress examined until fracture occurred. It is very remarkable that such extremely large crystals can be produced with comparative ease. As already mentioned, the number of crystals in the original sheet or bar, after the first "normalising" heat treatment, was about 150 to the linear inch. In the case of the sheet, in which the parallel portion is  $4 \times 1 \times 0.125$  of an inch, the number of crystals absorbed by the growing crystal must have been in the neighbourhood of 1,687,000. Indeed, since most of the single crystals grew well up into the shoulders of the test-pieces, the number must have been considerably more. In the case of the bars, 0.564 inch in diameter, where single crystals were obtained which occupied the whole of the region between the shoulders, *i.e.*, 4.5 inches (the parallel portion is 3.5 inches), the total volume of the crystal was rather more than 1 cubic inch since it grew well up into the shoulders at both ends. This must have been produced, therefore, from about 3,500,000 crystals. Finally, in the case of the bar, 0.798 inch in diameter, in which a crystal was obtained occupying the whole of the region between the shoulders, its volume was more than 2 cubic inches and the number of crystals which were absorbed in its formation must have been about 7,000,000.

An explanation of the experimental facts set forth in the present paper requires a completer knowledge of the aluminium crystal and the effect upon it of tensile stress than yet exists, but it is well that possible explanations should be considered even in the existing state of imperfect knowledge if only because the attempt will show in what directions further research is needed.

Crystals are usually classified according to their external geometrical form, to which their properties are found to be closely related. This method cannot be applied to determine the system to which metallic crystals, produced as above, belong, since they do not possess the external forms of crystals but take their shape from the test-piece in which they have grown. They are



allotriomorphic. Each crystal in the original sheet or bar, which contains 150 to the linear inch, has grown from a centre and its boundary is formed by contact with those of other growing crystals. As the rate of growth is not the same in all directions these boundaries are quite irregular in shape, but in an unstressed metal they are, broadly speaking, equi-axed, irregularly-shaped polyhedra. In spite of the absence of external geometrical form metallographic research has established the fact that these polyhedra are true crystals. In the original bar or sheet from which the stress due to working has been removed by preliminary heat treatment at  $550^{\circ}\text{C}$ ., these minute crystals are oriented at haphazard.

Hull\* has recently investigated the structure of aluminium crystals in a finely crystalline aggregate and concluded that the pattern thus obtained corresponds to a face-centred cubic lattice. Prof. Sir William Bragg has kindly examined several of the single crystals obtained in the sheets of the authors, and has come to the same conclusion. His experiments have removed all doubt as to the sheet being a genuine crystal, and have confirmed the view held by metallographists that etching is a reliable method of distinguishing crystals in a metal. Aluminium crystals, therefore, belong to the cubic system, and must have properties consistent with those of that group. The cubic system possesses the highest degree of symmetry, both external and internal. Investigations of the properties of crystals in this system indicate that the crystals are isotropic to the passage of light, heat and electricity, and expand uniformly in all directions. As regards elasticity, hardness and conduction of sound, it has been found that the values vary in different directions. These properties, however, are closely related to the symmetry, since maximum and minimum values have been found to coincide with axes of symmetry.

Differences of cohesion and hardness in different directions explain the variations in the tensile properties of the test-pieces which have been found. Although the single crystals obtained in the sheet have been formed in the same-shaped test-piece, their orientation relative to the stress obviously varied considerably, and may not have been precisely the same in any two of the cases tested. It will depend upon that of the crystal which grew. Both in the case of the sheet and the bar, the shape alters when stress is applied, since slip and deformation take place only on certain planes, and the changes in shape observed correspond to the attempt of the crystal to accommodate itself to the stress. Jeffries and Archer† have recently predicted what the shape of a square test-piece should be

\* 'Amer. Inst. Elec. Engineers,' vol. 38, Part II, October, 1919.

† 'Met. and Chem. Engineering,' vol. 21, No. 24, June 15, 1921.

after being pulled, supposing that this consisted of a single crystal, and that the planes of slip were at an angle of  $45^{\circ}$  to the stress. They concluded that the test-piece should be reduced in thickness in one dimension only, and that the fracture should be wedge-shaped. The bars tested by the present authors all show a wedge-shaped fracture, although there is every reason for supposing that the original orientations were not all identical, and this means that, under the stress, some of the bars must have altered their shape considerably in accommodating themselves to it. The extreme variations in ultimate stress found in single crystals produced in the sheet are 2.8 and 4.08 tons per square inch. It is somewhat surprising that the tenacity of the sheet, composed of 150 crystals to the linear inch, is not higher than 4.66 tons per square inch, for it has usually been supposed that metals owe much of their tenacity to the fact that they are aggregates of small crystals oriented at haphazard, and consequently that slip can only occur to a very limited extent in the planes of those particular crystals which happen to be oriented in the direction of minimum cohesion relative to the stress, and that the adjacent crystals thus support them.

The formation of the single crystals described in the foregoing paper does not differ in character, but only in degree, from the production of large crystals described by the authors in the previous paper.\* They were led at that time to put forward the suggestion that the crystals which grew were slightly more strained than their neighbours, because they had come to the conclusion that mechanical deformation supplied the energy for crystal growth, and that heat only permitted changes to take place which deformation rendered possible. Consequently, the more the crystals were strained the greater the energy they possessed. Mr. U. R. Evans, in a communication on the paper referred to,† suggested that it was to be expected that the less deformed crystals were the most active in crystal growth, and that the more strained crystals aligned themselves upon them. He also stated that growth appeared to depend more on the difference in the degree of deformation existing between certain crystals than on its absolute amount, although there appeared to be a minimum value below which no growth occurred. Mr. Evans' suggestion, however, is in conflict with the fact that as the deformation is increased the crystal size diminishes—in other words, growth starts from more, instead of fewer, centres. His suggestion requires the latter.

The question, however, cannot be satisfactorily settled until more is known of the changes which take place in a crystal when it is plastically deformed. Knowledge of this subject at the present time rests principally upon the

\* 'Journ. of the Inst. of Metals,' vol. 24, No. 2, pp. 83-131 (1920).

† 'Journ. of the Inst. of Metals,' vol. 25, No. 1, p. 299 (1921).

classical researches of Sir George Beilby. It appears, however, to the authors that the energy of growth cannot be stored in the amorphous vitreous films which, according to him, are the cause of work-hardness in metals, since the growth of single crystals in the aluminium sheet takes place at a considerably higher temperature than that at which the complete softening of the work-hardened metal is effected. Accordingly, all the vitreous amorphous metal must previously have recrystallised. It is, moreover, difficult to explain why the least deformation should produce the largest crystals on heating if growth depends on the presence of amorphous metal. Sir William Bragg has kindly agreed to collaborate with the authors in a joint investigation of this question, and they are hopeful that, as a result of the X-ray analysis of large crystals, such as their experiments have rendered available, which can be strained to any required extent, it will be possible to ascertain what happens to the arrangement of the atoms in the space lattice under these conditions. If this is the case, it is almost certain to throw light on the cases of crystal growth recorded in the present paper. In the meantime and with a view of meeting Mr. Evans' criticism, it may be suggested that, instead of a more highly energised crystal growing direct, it deposits first of all a new crystal nucleus; in other words, a very limited form of recrystallisation takes place. This new crystal is by hypothesis quite free from distortion and can absorb all the strained crystals in the test-piece. Against this view may be urged certain objections based upon experimental facts observed in the research.

1. If a test-piece consisting of a single crystal is stressed so as to produce an extension of 2 per cent. on 3 inches, this is insufficient to enable it to re-crystallise on heating at  $550^{\circ}$  C. or even at  $600^{\circ}$ . It is probable, therefore, that this treatment is not sufficient to enable crystals in a crystal aggregate to re-crystallise.

2. When a sheet or bar is heated at  $550^{\circ}$  after being rolled it re-crystallises in about 1 hour and after that little change is evident for some time. If the heating is continued for 24 hours or several days, according to the purity of the metal, large crystals form which originate at the surface and sometimes grow right through the sheet. There is no evidence of spontaneous re-crystallisation having taken place, and it is possible that the surface was in a state of some strain following on re-crystallisation and that a few crystals grew in consequence. This case is very similar to that in which large crystals are produced by slight straining followed by heat and it seems probable that the cause and method of growth are the same.

3. The relations observed between crystal size and temperature for the same degree of deformation are the reverse of what is usual. In cases where

there is no doubt that re-crystallisation has taken place, the higher the temperature of heating the larger are the new crystals.\* On the other hand the single crystals produced by the authors are formed at the lowest temperatures at which growth occurs and if the temperature is raised the crystals become smaller for the same degree of deformation. This was shown quite conclusively in their previous paper.† The raising of the temperature is equivalent to increasing the deformation and the smaller crystal size is due in both cases to growth starting from a larger number of centres. Moreover, unlike the crystals ordinarily produced by re-crystallisation, these large crystals do not grow at one another's expense. It appears as if the number of centres from which growth starts determines the number of crystals in the final state.

The authors are extending their experiments on the production of single crystals to other metals. They desire to acknowledge the valuable assistance of Mr. H. M. Chapple in carrying out the tensile tests.

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*Address of the President, Prof. C. S. Sherrington, at the  
Anniversary Meeting, November 30, 1921.*

Since the last Anniversary Meeting the roll of the Society has lost by death fifteen Fellows and one Foreign Member :

Sir William Abney.	Lord Moulton.
Mr. Spencer Pickering.	Prof. A. W. Reinold.
Dr. A. Muirhead.	Prof. E. J. Mills.
Sir Lazarus Fletcher.	Colonel J. Herschel.
Prof. W. Odling.	Mr. G. W. Walker.
Prof. L. C. Miall.	Dr. H. Woodward.
Prof. R. B. Clifton.	The Earl of Ducie.
Dr. F. A. Bainbridge.	

On the Foreign List

Prof. G. Lippmann.

The Anniversary Meeting affords appropriate opportunity for some spoken reference to them.

The earliest loss was that of WILLIAM DE WIVELESLE ABNEY, a Fellow of

\* Mathewson and Phillips, 'Trans. of Amer. Inst. Mining Engineers,' vol. 54, pp. 1-50 (1916).

† *Loc. cit.*, pp 117-119.

the Society for upwards of forty years. Much of his scientific work may be summarised as being the establishment, by experiment, of photography as a science. With Sir William Abney photography was not merely a means but in itself a scientific end. The building of the image both in the wet and in the dry plate were successfully studied by him. He was a pioneer in the photography of the infra-red region of the spectrum. He suggested more than forty years ago the charging of carbons with calcium salts to enhance the arc-light beam, the flame arcs of to-day. Later he passed, so to say, from the photographic plate to the retina and investigated the relative visual intensity of different portions of the spectrum. As Advisor to the Board of Trade he obtained, partly in collaboration with the late W. Watson, data most valuably discriminating between various types of colour vision; he contributed accurate measurements of visual differences between the foveal and para-foveal regions of the retina. His measurements of the visual luminosity curve of the spectrum stand as classical data of reference. He is remembered in the Society as a man whose personality endeared him to everyone who knew him.

The death of SPENCER PERCIVAL UMFREVILLE PICKERING removed a chemist, who at the time of his election to the Society, was one of the most arduous and prolific of researchers. The main theme of his work was solution and hydrates. A man of original view he often collided rather than moved with the scientific trend of the time, but he spared himself no pains in the pursuit of observations. His association with the Society will be happily perpetuated by the bequest from him, to become a research fund bearing his name.

ALEXANDER MUIRHEAD, whose name is connected with the duplexing of submarine cables by the artificial line with distributed capacity, also contributed perseveringly to the practical establishment of electrical standards of capacity. Much of his work was accomplished against difficulties of health which would have disheartened any but a man of remarkable courage and resolution.

LAZARUS FLETCHER was for ten years Director of the Natural History Museum. Mathematically trained, his chief scientific interest lay in problems connected with the physics of crystals, though much of his time was given to the great National Collection of minerals of which he had charge for nearly thirty years. He devoted much patient and accurate research to the meteorites in that collection. His papers that are probably best known are those on the dilatation of crystals by heat, and on the Optical Indicatrix and transmission of light in crystals. In the latter of these he showed how the optical characters of crystals could be simply

developed from the geometrical properties of an ellipsoid (which he called the Indicatrix) independently of any hypothesis as to the nature of the ether. His method has now been adopted by almost all teachers of the subject. Those who knew Sir Lazarus Fletcher are not likely to forget his simplicity of manner, his quiet humour and his unfailing consideration for others.

WILLIAM ODLING, for many years Professor of Chemistry at Oxford, died there this spring at the age of ninety-two, severing a link with the chemistry of the mid-Victorian time. It was under his Chairmanship of the Institute of Chemistry that that body was granted its Charter in 1885.

LOUIS COMPTON MIALl was a biologist; a naturalist in the old sense of the word. He did good and lasting zoological research. He was one of a group, few in number but strong in personality and influence, who laid the foundation of the existing University of Leeds. He was an enthusiastic educationalist, and appreciated highly the calling and the opportunities of the primary school-teacher; he helped that calling in many ways. He himself was a strikingly successful teacher. Those who knew him will recall how he studied teaching as an art, and loved it for its own sake.

Dying at Oxford a little later in the year than Prof. Odling, ROBERT BELLAMY CLIFTON had been Professor of Experimental Philosophy there from 1865 until 1917. His first duty for his Chair had been the superintendence of the erection of the laboratory, the Clarendon Laboratory, of which Sir Richard Glazebrook writes in his obituary notice of Clifton: "it was the first built in Europe for the special purpose of experimental instruction in Physics." The fittings and teaching apparatus were largely to Prof. Clifton's designs, and he gave much time and thought to their construction, perfecting and re-perfecting them in detail. So strict a custodian of them did he become that it was sometimes humorously said they had become too precious to be very accessible for their original purpose. However that may be, under his hospitality the laboratory he had erected gave a home to a great piece of experimentation in Prof. Boys' determination of the gravitation-constant. Clifton was a man of genial personality, of much conversational gift, shrewd and humorous, and of a nature full of kindly qualities.

WILLIAM REINOLD was Professor of Physics in the Royal Naval College. He had been Demonstrator under Clifton in the Clarendon Laboratory. It was during his long activity at the Royal Naval College, and as a teacher there, that his main scientific life-work was accomplished.

In March last died suddenly Lord MOULTON OF BANK. Not an actual investigator in Science, he was yet a very real servant to the cause of scientific progress in this country. He possessed remarkable power of acquisition of knowledge, seizing rapidly and broadly the lines of advance

taken by knowledge. A facile expositor of scientific themes to a lay or semi-lay audience, and gifted with an enthusiasm that never failed, he promoted the public appreciation of scientific work. Foreseeing from the outset of the War the magnitude of the strain that it would involve, he had the courage to demand a mobilisation of scientific resources adequate to that strain. The country owed much to his insistence and unsparing effort. His was a virile persuasion. After the coming of the Armistice, he turned his energies and influence toward urging a more thorough liaison between science and the industry of the country.

EDMUND JAMES MILLS held the Young Chair of Technical Chemistry in the Glasgow and West of Scotland Technical College. His papers were numerous both on applied and theoretical chemistry, and not a few of them were contributed to this Society, the first of them now more than fifty years ago. Returning to London in later life, he was for many years a frequent attendant at the Society's meetings.

Colonel JOHN HERSCHEL, a son of Sir John Herschel, and at one time Deputy-Superintendent of the Great Trigonometrical Survey of India, had been a Fellow of the Society for fifty years. He was a spectroscopic observer of a solar eclipse as far back as 1868.

GABRIEL LIPPMANN, the eminent French physicist, died while at sea on his way from Canada home to Paris. He had been a Foreign Member of the Society for five and twenty years. His interest in physics lay largely in the philosophic aspect, though his name is most familiar in connection with the capillary electrometer and with colour photography. Lippmann's capillary electrometer became, so to say, a household tool in every physical laboratory, and likewise in many biological laboratories. In animal physiology it proved of unique service for the observations of the slight and fleeting electromotive reactions of isolated nerve and muscle. Until the advent of the string galvanometer it was the only instrument which could really cope with them.

Of Lippmann's process for the reproduction of colour by photography, our Foreign Secretary, Sir Arthur Schuster, who knew him from a time when they were fellow students together, kindly writes me as follows:—"Lippmann's work on colour photography well illustrates his great experimental skill. Independently of the late Lord Rayleigh, who, in 1887, had on theoretical grounds foreseen the possibility of the reproduction of natural colours by an interference method, Lippmann conceived the same idea; but the experimental difficulties were formidable. The method depends on establishing a periodic structure in a photographic film by the interference of the direct light and its reflexion from a metallic surface. It was neces-

sary for the purpose that the films unlike those in ordinary use, should be transparent. The production of such films appeared for many years to be an insoluble problem, but ultimately the difficulty was overcome, and in 1901 Lippmann obtained his first success; but it was several years before he could secure the equality of sensitiveness throughout the visible spectrum which is essential if the natural colours are to appear with their correct values. The photographs obtained by Lippmann cannot be reproduced in print, but may be shown with brilliant effect by projection on a screen."

GEORGE WALKER WALKER had, following on a career of high promise at Cambridge, been successively Lecturer in Physics at Glasgow University, Superintendent of Eskdalemuir Observatory, Director of the new Magnetic Survey of the British Isles, and finally chief scientific worker at the Royal Naval Mining School, Portsmouth. It was during work in that latter capacity that his fatal illness began. He united in a remarkable degree mathematical attainment and inventive capacity. By his death physical science lost, sadly early, a finely accurate experimental exponent.

HENRY WOODWARD, late Keeper of the Department of Geology of the Natural History Museum, was a distinguished paleontologist. His scientific reputation was especially as an authority on extinct representatives of the Crustacea. He was one of the founders, and for over fifty years editor, of the 'Geological Magazine.' His example and personal contact were a stimulus to many others, and the encouragement given by him to amateur workers was one of the features of his official career.

FRANCIS ARTHUR BAINBRIDGE died last month in early middle age. He had been elected a Fellow in 1919. Of delicate physique, constantly struggling against ill-health, he nevertheless accomplished, besides much routine teaching, a great deal of accurate research, some in pathology, more in physiology. He contributed to the differential recognition of the several types of paratyphoid bacilli, a matter at once of theoretical interest and great practical importance. His work in physiology opened with investigation of lymph formation, following on that of Bayliss and Starling. Then came work on urinary and salivary secretion, all of it characterised by great clearness of objective, and definiteness of plan. One of his best papers is one of his most recent. Its subject is the acceleration of the pulse, which muscular exercise constantly and so quickly induces. Bainbridge showed that the increased filling of the venous chamber of the heart, and the consequent increase of pressure in it, itself acts as a stimulus which excites through the nervous system the more frequent beating of the heart. He traced this control in part to depression of the vagus, partly to stimulation of the nerves which accelerate the heart. Bainbridge was an



experimentalist of exceptional dexterity. Always cheerful, he seemed at his cheeriest when busiest in the laboratory.

LORD DUCIE, whose decease fell latest in the year, had been a Fellow for nearly 67 years. Interested in Science, he was also greatly interested in secondary education. Latterly he had given his time and abilities chiefly to the countryside where he resided. By virtue of the date of his election to the Society, 1855, he had become its Senior Fellow.

We may note that the Seniority of Fellowship of the Society has now passed to one who has been a member of Council on many occasions, a Foreign Secretary, and Secretary, our sometime President, Sir Archibald Geikie, known among us also as the genial historian of the Royal Society Club.

It is little more than two years since the death of the late Lord Rayleigh, and this afternoon in Westminster Abbey there has been unveiled the tablet to his memory, given by subscribers from this Society and from the University of Cambridge, of which he was Chancellor. At the presentation ceremony the Society and the donors generally were represented by the Chairman of the Memorial Committee, Sir Joseph Thomson. The Society will feel it peculiarly appropriate that their representative on such an occasion should be one so closely associated with the late Lord Rayleigh in the Society, in the University which was their common *alma mater*, and in the domain of physical science itself. The recollection of the late Lord Rayleigh's personality is present with us all: to meet him was to receive the impression of true greatness. The legend on the mural tablet runs:—*"An unerring leader in the advancement of Natural Knowledge."* To-day has seen the fulfilment of a fitting tribute, in a fitting resting-place, to a memory veneration for which the lapse of time will but intensify.

The Bakerian Lecture of the year was by Dr. T. M. Lowry and Mr. P. C. Austin on "Optical Rotatory Dispersion." The Croonian Lecture was by Dr. Henry Head. It had for its theme the disturbance of action in the nervous system due to the impairment of one part reacting on the function of another. Not unnoteworthy concerning the lecture is that, to push further the enquiries underlying it, the lecturer had subjected to surgical severance and restitching nerves of his own arm.

To Dr. Head the Society owes a most acceptable gift. The Society possessed no portrait of Lord Lister. Dr. Head, on learning this year that such was the case, offered to the Society a portrait of Lister, by Legros, in black and white, a portrait that had been given to Dr. Head by the poet Henley, in whose possession it long was,—Henley, the poet whose word-portrayal of Lister, under whom he was a patient, is extant in the famous sonnet familiar to us all. The gift was gratefully accepted by Council.

The Anniversary Meeting is naturally an occasion for retrospect; it is also one which invites some thought to the present. The present time has in it an element of considerable anxiety for those who regard the prosperity of Science. Although the recent past has, it is true, been not unfavourable.

I mentioned just now a university building, the earliest constructed for systematic experimental teaching in Physics, and that just 50 years ago. It is a satisfaction to note the multiplication of such laboratories since then. This year at the inauguration in London of the Institute of Physics Sir Joseph Thomson remarked that now, in contrast against the early years of the Cavendish Laboratory, the study of Physics, as regards the numbers to whom it gives opening for a livelihood, constitutes in fact a profession of its own. The same can be said of the Science of Chemistry, and of the Biological sciences. Cultivation of science has been a feature of the country's progress. This has in part been adjunct to the movement for the foundation of new Universities. The number of the English Universities has doubled in the last quarter of a century. The new Universities have shown admirable energy in their departments of science. Following in the tradition of the best of the older Universities they have, in instance after instance, made their laboratories places of research. Only last year the Council of the Society stated that to increase the resources and equipment of the Universities is one of the best ways of aiding research in pure Science. The Report of the University Grants Committee in February of this year indicated that the Universities were unable to meet their existing responsibilities, and that their resources are inadequate to meet legitimate demands upon them. It is, therefore, a matter of grave concern that the Government Grant to the Universities is now to be cut down heavily. The maintenance of the Universities at the level of efficiency which they have struggled so resolutely, and with much service but poorly paid, to sustain, will thus receive a very severe blow.

Regression is the more disappointing because, during the war, there came an awakening of the conscience of the nation in regard to Science. The national need for wider and deeper interest in, and understanding of, Science came home to the community as it had not done hitherto. The importance to the nation of, for instance, the national Physical Laboratory, whose parent this Society may justly claim to be, began to receive more general recognition than before. Its importance to the State became cogent to the State. Six years ago saw the founding of the Advisory Council on Research to the Privy Council, and a year later the establishing of the Department of Scientific and Industrial Research. These were not created as part of the machinery for the war, though during that common need they, like every other

national organization, made their contribution. They were brought into existence to remedy deep-seated shortcomings which the war revealed in the country's organization for scientific research. Their full effect was only to be expected to come now, after the attainment of peace. It is, therefore, gravely disquieting that their State support estimates are being now reduced by some 30 per cent. and that further reduction still is asked for.

Again, if we turn to the domain of Biology, and take within that the field of Medical Science, the Medical Research Committee, as it then was, had been organised and started not long before the outbreak of the war. It had from its beginning shown its utility and brought evidence of the great field of usefulness before it. Its services during the war and since the ending of the war have been conspicuous, indeed inestimable. Public appreciation of it has enhanced. The Government has recently raised the status of the Committee, so that it is now the Medical Research Council under the Privy Council. Annual Reports indicate the quality and the volume of the work it is accomplishing. It is creating a new era of research in scientific medicine in this country. But its financial State aid is to be cut down for the coming year, and the extent of that reduction is a real anxiety to all who have at heart the progress of Medicine in this country and of the Sciences on which Medical Science itself rests.

I may say that, broadly taken, the apparatus for prosecution of research in this country is made up as follows: (1) Scientific and Professional Societies and some institutions entirely privately supported; (2) Universities and Colleges, with their scientific departments; (3) Institutions, using that term in the widest sense, directly subventioned by the State, such for instance as the Medical Research Council, the Development Commission, and the Department of Scientific and Industrial Research. Of these three categories, the first named, the Scientific Societies group, work without financial aid from the State, apart from the small though extremely useful two Government Grants distributed, mainly to individual workers, through this, the Royal Society. At the present time many of the Societies sorely need financial help to carry on their labours, and some are absolutely at a loss to know how to publish the scientific results that are brought to them. (2) The second category, the Universities and Colleges, depend in part upon Government aid. In the aggregate of twenty-one institutions of University rank, following Vice-Chancellor Adami's figures, students' fees and endowment provide about 63·5 per cent. of the total income; for the rest they are dependent on Government Grant. (3) The third category as said, draw State-support direct.

This triple system may seem a somewhat haphazard and inco-ordinate

assembly. Yet in reality it is an organisation with much solidarity, and its co-ordination is becoming more assured. Its parts dovetail together. The first group, the scientific and professional Societies, is provided with a medium of intercommunication and co-action, the Conjoint Board of Scientific Societies. As to the separate categories composing the triple system itself, they also are in wide touch one with another. Between the Scientific and Professional Societies on the one hand and the Universities on the other, contact and inter-relation are secured by some degree of free and rightful overlap, both as regards general subject matter of research and of their *personnel*. Finally, there is excellent contact between both these categories and the third, the State-subsidised institutions. A special feature of the policy and administration of these State organisations secures this, a feature which makes the whole of this subject the more cognate to the purview of our own Society. To exemplify I may turn, for instance, to the Development Commission. Its programme of Fishery Research, avoiding the terms "pure" research and "applied" research, in view of the possible implication that pure research does not lead to practical result, directs research not alone to the solving of particular economic problems. It supports more especially what it terms "free" research, investigation in this case of the fundamental science of the sea and of marine life. This term "free" research is set in its full light by words of the Lord President of the Council, Mr. Balfour, where he points out that while the State may aid research, it will only destroy research if it resolves too rigidly to control it.

Again, with the Advisory Council of Scientific and Industrial Research, its programme, gradually defined during the past six years, is laid down as having four main points: (1) the encouragement of the individual research worker, particularly in pure science; (2) the organisation of national industries into co-operative research associations; (3) the direction and co-ordination of research for national purposes; (4) the aiding of suitable researches undertaken by scientific and professional Societies and organisations. It recruits researchers by giving financial opportunity to promising students to be trained in research attaching them to experienced researchers. In short, it apprentices to research a number of selected younger workers in Universities, Colleges, and other institutions scattered throughout the country.

So, similarly, the Medical Research Council. Its Secretary, Sir Walter Fletcher, in an illuminating presidential address to Section I of the British Association Meeting this summer, said, speaking of the nexus between scientific research and the progress of Medicine, "It is the accumulating knowledge of the basal laws of life and of the living organism to which

alone we can look for the sure establishment either of the study of disease or of the applied sciences of Medicine."

It is evident, therefore, that with a policy based on such principles as these, the third category in the triple system constituting the organisation for scientific research in this country, is one which has common aim and solid touch with both the others, the Universities and the Scientific and Professional Societies. One sees in short that the organisation which has come into existence and is maintaining scientific research in this country, is a real organisation. It did not spring fully equipped from the head of Jupiter. It has grown up rather than been planned. In that respect it is an organisation essentially British, and it seems qualified to do its work for the country well. We hear of adventures, political and other, the offspring of the day. But these were no adventures, these, to my mind, welcome, long-overdue, steps forward by the State toward the succour of Science and its welfare, steps that help to strengthen and consolidate the organisation for research by such adjuncts as the Medical Research Council and the Department of Scientific and Industrial Research. One of the strengths of this organisation that has arisen is, in my view, that it interlocks with the educational system of the country. It is an organisation which proceeds on the wise premiss that, in the case of Science, the best way to get the fruit is to cultivate the tree. It is an organisation which is proving successful and economical. Its output has proved a more than liberal return on the funds at its disposal.

But essential to its own continuance is continuance of adequate financial support from the Government. A tripod cannot stand upon two legs. The State-contribution in this country is relatively not large, but it is most important. Important as it has been in the past, it has now an importance most especially great. The cost of investigation is now higher, much higher than it has been. Endowment funds carry less far than they did carry. Private benefactions and voluntary generosity, although willing, are less able to be found and less capable at this time; already gauged as inadequate of themselves alone before the War, they obviously cannot alone cope with the necessary undertakings now. The present is a time when a large-scale withdrawal of the Government's financial support must prove most formidably crippling. Such crippling will be greater than the actual measure of the sum withdrawn would entail in ordinary times.

None can fail to see the urgent need for national economy. It may be objected that the plea to which I am speaking is, in fact, one for the preferential treatment of Science. That is not so. Faced with need for stringent economy, there must, of course, be a rigorous cutting down of

expenditure that is unnecessary. But a first enquiry is the discrimination between expenditure upon the inessential and the essential. Otherwise the economies seemingly effected may be no economies. The savings may be made in a fashion most costly in the end. Conceded that there must be some reduction in the moderate State expenditure on research, it would be no true economy if that reduction were pushed to the point of causing collapse of the fabric for the production of much-needed knowledge or of whole compartments of that fabric.

The necessary supply of trained research workers cannot be retained or replenished except by a steady policy pursued. If the financial provision for research is too severely cut down, that will mean the extinction of various investigations which cannot be satisfactorily continued at all under narrower limits of expenditure than are imposed at present. One feature of modern research is that it has become more largely team-work, the combined effort of an assorted group of individuals with special training. Want of volume has tended to be a weak point in our national research. Reduction of the support by Government will react most rapidly on the number of competent investigators available, the number that makes a fair volume of team-work possible. The Report of the Advisory Council states that the effect of a setback of this kind will be long-continued and adds that it may be lasting.

To pull down under emergency what has been built up through years of careful experience and is proving efficient, can hardly be ultimate economy. It is to unlearn a useful lesson learnt. Curtailment of the State aid—relatively small in this country—given to scientific research must harm the scientific production of the country. Some curtailment, however, at this time seems unavoidable. Though extension of buildings and equipment and *personnel* is wanted, it may be necessary to withhold that extension at this time, maintaining broadly the *status quo* ready for expansion when that is once more feasible. But if research be an indispensable factor in the rebuilding of the national life, sacrifices should not be required from it disproportionately greater than from other services of a similarly essential kind. Reduction of the State's support on a scale to entail ruin to the existent organisation would be a wastage rather than an economy. Calmly viewed, what more reminiscent of the wastage of the War itself than for machinery actually constructed, assembled, and producing what is needful for a nation's strength as a pillar in the industrial and intellectual temple of the world, to be now under temporary change abandoned or broken up; and at a time when industry as a whole stands convinced of scientific research as a necessity for its recovery and well-being.

My hope would be that scientific research on its present maintenance will

be considered part of the intellectual bread of the community, part of the bed-rock on which rests the efficiency, not to speak of the industrial equipment of the nation; that it will be treated as such in the measure of State-support continued to it; that the State will remember that that support has to embrace at least both the Universities on the one hand, and, on the other, the research institutions administered by the State, for this reason, namely, that the country's organisation for research, complex in origin, yet economical and effective, stands as an integral system, to whose entire existence is essential an adequate State provision for both these constituent elements, indispensable, since they are, to the whole structure of the system.

I now proceed to the distribution of the Medals.

The Copley Medal is awarded to Sir Joseph Larmor.

Sir Joseph Larmor has long held a leading position in the British School of Mathematical Physics. There is hardly a branch of this subject to which he has not made contributions of distinct originality and great value. His earlier researches on Dynamics, on Optics, both geometrical and physical, and on Elasticity, are marked by keen insight and by the novelty introduced in the treatment of familiar subjects. In more recent periods he has written on problems of Geodynamics, with the same illuminating force. His contributions to the Theory of Electricity, in its many ramifications, are numerous and profound. His treatise on 'Æther and Matter' forms a distinct landmark in the history of the subject. In this we have the foundation of electromagnetic theory on the single principle of least action, with the electron taken into account as an æthereal structure. He was the first to establish (to the second order of velocity) the correspondence between moving and fixed electrical systems, and shares with Lorentz, the distinction of discovering the generality of this correspondence to any order. It may fairly be said that his preliminary work was of the utmost value in paving the way to the modern developments of the Theory of Relativity. In addition to his own researches Larmor has, as Lucasian Professor, stimulated the work of others with notable success. His intimate and extensive knowledge of the history as well as of the results of physical science marked him out as the appropriate editor of the works of Stokes, Kelvin, James Thomson, and Henry Cavendish, to which he has contributed most serviceable annotations.

A Royal Medal is awarded to Dr. Frederick Frost Blackman.

Dr. Blackman is distinguished for his contributions to plant physiology, and especially to knowledge of the process of photo-synthetic assimilation of carbon dioxide. In this connection he devised apparatus of great delicacy and

accuracy. Later he proceeded to an exhaustive investigation on the rate of assimilation within the green leaf. He determined, under varied and controlled conditions, the inter-relationship of the external factors and their several and joint effects on the rate of assimilation, and has laid the foundation on which a good deal of subsequent work by other investigators has been rendered possible.

He was thus led to his theory of limiting factors, which has exerted much influence in both plant and animal physiology. With the help of his co-workers he has importantly extended our knowledge of permeability, and of the influence of anæsthetics on plants. He occupies a leading position amongst plant physiologists, not only by reason of the importance of his discoveries, but also on account of the effective stimulus he has given to the school of investigators who have been trained in his laboratory.

A Royal Medal is awarded to Sir Frank Watson Dyson.

Sir Frank Dyson is distinguished not only for his enlightened and energetic administration of the Royal Observatory, but by his many important contributions to Astronomy. He has devoted special attention to investigations of the movements and distances of the stars, and of the bearing of these upon the structure of the stellar universe. He has concentrated his energies particularly on the stars surrounding the north celestial pole, and has collected or determined for this region of the sky all the different data which seem likely to aid in the solution of the stellar problem. In a long series of papers he has shown himself able not only to conceive and execute large schemes of observation, but also to deduce by graphical and mathematical analysis the theoretical conclusions which are implicit in the mass of data. Some of his investigations are remarkable for the extensive data which have been utilised; one of them involves the proper motions of 12,000 stars, and another of 26,000 stars. These researches have given Sir Frank Dyson a place in the front rank of workers on stellar distribution and movements.

He has also given much attention to the accurate determination of stellar magnitudes, and has successfully established a regular programme of work on stellar parallaxes which has yielded results of high precision for a large number of stars.

Previous to this he had been conspicuously successful in obtaining records of the spectrum of the corona and chromosphere during eclipses of the sun; his publications on those subjects are among the most valuable sources of solar spectroscopic data. It was mainly to his foresight and organizing ability that we owe the successful observations of the deflection of light by the sun's gravitational field during the eclipse of 1919.



The Davy Medal is awarded to Prof. Philippe Auguste Guye in recognition of his work on optically active organic substances, on molecular association and on atomic weights.

In his early work on Organic Chemistry, Prof. Guye was led to investigate the question whether a quantitative relationship exists between the molecular rotations of optically active substances and their chemical constitution. Although the answer proved to be in the negative, the attempt to establish such a relationship was yet productive of much valuable research on optical isomerides in his own laboratory, and stimulated the efforts of many investigators in that branch of physical chemistry, particularly in this country.

Shortly after he had put forward his theory of the "product of asymmetry" he was attracted by the problems connected with Van der Waal's equation and the critical state, and, from his interest in these, two important lines of investigation opened out. The one had relation to the degree of molecular complexity of matter in the liquid state, and occupied his attention mainly between the years 1893 and 1911. The other led him at the beginning of the present century to advocate, with much energy and persistence, the advantages of the physical method of determining atomic weights. In this field of work he became one of the foremost investigators; his work on the calculation of precise gas densities was followed by chemical studies of the atomic weights of nitrogen, silver and chlorine, and by inquiries into sources of error, hitherto little recognised, in atomic weight determinations.

The Hughes Medal is awarded to Prof. Niels Bohr.

Prof. Bohr is well known to all physicists as the author of the conception to which the name "Bohr-atom" has been attached. A decade ago it became clear, from the researches of Sir E. Rutherford and others, that the atom of any element is formed out of an excessively minute positive nucleus of electricity, round which circulate a number of negative electrons equal to the atomic number of the element. Bohr discovered a mechanism for the motion of these electrons, which solved immediately the long-standing puzzle of the Balmer series of hydrogen, and which, after development and discussion, appears likely to provide a complete explanation of the spectra of the various elements. In this way he has opened up a line of investigation which has already attracted to itself many of the ablest mathematicians in Europe, and of which the success, in the simplest cases of the two light elements hydrogen and helium, is even now little short of perfect.

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# *The Aurora Line in the Spectrum of the Night Sky.*

By LORD RAYLEIGH, F.R.S.

(Received November 15, 1921.)

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### § 1. *Introduction.*

Several observers have found that the green line of unknown origin seen in the Aurora Borealis can also be seen in the sky on ordinary nights, and in comparatively low latitudes.\*

Slipher, in particular, has studied the line photographically, and has succeeded in recording it with a three-prism spectrograph of 15 inches focus, thus obtaining a good measurement of the wave-length.

The present paper details further and perhaps more systematic observations on the occurrence of this line in the sky on ordinary nights. The primary object was to determine whether or not the phenomenon was to be classified with the polar aurora. If so, it might be expected that every gradation of intensity between this usually very faint effect and a bright auroral display would be met with. It might also be expected that this effect would become more pronounced as the observer moved northwards.

Other questions of interest were whether or not the intensity of the spectrum line was connected with magnetic or solar disturbance.

It does not appear that any photographs of the auroral spectrum, whether on ordinary nights or on nights of a display, have previously been made in this country.

The spectrographs used were provided with Dallmeyer cinematograph lenses working at F/1.9. These lenses have proved satisfactory for the purpose, the definition and field of view being all that was required. There is no advantage in making the collimator of short focus, and a simple achromat of 9 inches focus was used.

\* Weichert, 'Phys. Zeit.', vol. 3, p. 366 (1902); Campbell, 'Lick Obs. Bulletin,' vol. 5, p. 46 (1908); 'Astr. Soc. Pacific,' vol. 29, p. 218 (1917); Slipher, 'Astrophys. J.,' vol. 49, p. 266 (1919).

Two instruments were constructed. No. 1 had a Rutherford compound prism, and gave a scale of 358 Ångström per millimetre near the green line, No. 2 had a simple 60° prism, and gave a dispersion about two-thirds of the previous. This scale, though small, is quite adequate to the purpose of diagnosing the presence or absence of the green line. Large relative aperture is essential to the work, and, if the prism is to be of moderate size, it entails short focal length and small dispersion. The standard width of slit used was 0.12 mm.

The plates used should be those sensitised with erythrosin, such as are supplied by most makers under the name of isochromatic or orthochromatic. These have a rather narrow but high maximum of sensitivity in the green, situated near the aurora line, and are thus very favourable for the purpose. In this connection, it should be noticed that, if too wide a slit or too small a dispersion is used, there is a possibility of mistaking this maximum in the continuous spectrum in the sky for the aurora line itself.

"Panchromatic" plates, sensitised with the various cyanin dyes (pinacyanol, etc.), are not nearly so good as the erythrosin plates for this special purpose, and much time was lost in attempting to use them.

It is always necessary to put a comparison spectrum on the plate, if only to guide the eye where to look for the green line, if present. Without such guidance, there would be constant danger of missing a faint indication, or of mistaking an accidental marking for one.

When at home, I have used a krypton tube for the comparison, the green krypton line at 5570 (which has been thought by some to be identical with the aurora line) serving for reference. When away from home, to save the trouble of carrying an induction coil, it has been found convenient to use a spirit lamp, with calcium chloride on the wick. This gives the calcium band 554, which is near enough to serve as a reference mark. The usual occulting slit arrangement was used for the comparison.

The exposure to the night sky can be begun as soon as it is dark. To avoid the necessity of being present to close the instrument before dawn, it has been found convenient to do this automatically. A photographic shutter of the roller-blind (Thornton Pickard) type is fixed in front of the slit, and should have a large enough aperture to allow of adjustment of the slit through it: otherwise the shutter must be removable for access to the slit. In any case, the cover of the slit can be shifted, after the comparison spectrum has been put on, by a forefinger, introduced through the opening of the shutter. The shutter is set open, and the lever which releases it is attached to the hammer of a cheap alarm clock by means of a thread, which is stretched by moving the clock laterally till on the point of

releasing the shutter. The bell of the clock is of course removed. When the alarum mechanism works, the shutter is automatically closed.

A little easing of the mechanism of the shutter may be needed, and it may be advisable to prolong the lever of the shutter, attaching the thread to the end of the prolongation. A perfectly trustworthy arrangement can readily be made in this way. Sand clocks and water clocks have been tried, but experience has been in favour of the alarum clock as described.

The instruments were always pointed approximately to the north at an elevation of  $45^{\circ}$ .

### § 2. *Intensity in Relation to Magnetic Disturbance.*

Exposures were made every night with the Rutherford prism spectrograph (No. 1) and a Marion "Iso-record" plate from February 26 to July 3, 1921. Satisfactory records were obtained on 145 nights. In the few remaining instances the photograph was a failure from accident or inadvertence.

These photographs were used for establishing the intensity of the aurora line. It would have been more satisfactory to have some definite method of photometry instead of an eye-estimate, but, on account of the faintness of the effect, this did not seem practicable. The classification was thus:—

2 denotes a strong impression.

1 a definite though faint impression.

0 no impression of which I could be sure.

This classification is, of course, rather arbitrary, particularly as regards the borderland between 2 and 1. It was found, however, that when the whole series was re-examined without reference to the original classification, the new intensity figures assigned were nearly always the same as the old.

There are other circumstances which complicate the interpretation of these intensity figures. Moonlight within a few days of full moon gives a background of continuous spectrum, which tends to mask a feeble indication of the aurora line. Again, a stronger effect may be expected on clear than on cloudy nights. It would be very difficult to make a satisfactory allowance for this. Sometimes, however, the aurora line was of intensity 2 on cloudy nights, suggesting that the action of the clouds is rather to diffuse than to absorb the light of the aurora line; and this makes little difference, the source being diffuse already. On really dark nights the clouds are heavy enough to absorb nearly all light, whether of this kind or of any other. But such very dark nights are not numerous.

Again, the exposures were shorter during the summer months, being necessarily limited to about 4 hours at midsummer. It would be possible to

limit the exposures to this at all seasons, and in a future series this should be done. But the present series was begun without any knowledge of what would be encountered, and naturally without a very definite programme. Consequently, in winter and spring the full hours of darkness were utilised for the exposure.

In spite of these various complications, it is believed that the recorded numbers indicate the daily variations of the auroral intensity well enough for a useful comparison with the degree of magnetic disturbance. This latter has been very kindly furnished to me by Dr. C. Chree, F.R.S., from the Kew Observatory records. Dr. Chree assigned character figures, 2, 1, 0, according to the degree of magnetic disturbance. The figure has reference to the general magnetic character for the eight hours centred at midnight, and thus corresponds roughly to the actual time while the exposure is proceeding.

The records for auroral intensity and magnetic disturbance are given below :—

Date.	Aurora line.	Magnetic character.	Date.	Aurora line.	Magnetic character.
February 26 .....	2	0	April 3 .....	—	1
" 27 .....	1	1	" 4 .....	—	0
" 28 .....	1	1	" 5 .....	0	0
March 1 .....	1	1	" 6 .....	1	0
" 2 .....	0	1	" 7 .....	2	0
" 3 .....	0	1	" 8 .....	2	0
" 4 .....	0	0	" 9 .....	1	1
" 5 .....	0	0	" 10 .....	1	1
" 6 .....	1	0	" 11 .....	2	1
" 7 .....	0	1	" 12 .....	2	1
" 8 .....	0	0	" 13 .....	0	1
" 9 .....	1	2	" 14 .....	1	1
" 10 .....	2	0	" 15 .....	—	1
" 11 .....	1	0	" 16 .....	—	1
" 12 .....	0	0	" 17 .....	2	0
" 13 .....	1	0	" 18 .....	1	2
" 14 .....	2	1	" 19 .....	1	0
" 15 .....	2	1	" 20 .....	0	2
" 16 .....	0	0	" 21 .....	0	1
" 17 .....	—	0	" 22 .....	2	2
" 18 .....	2	0	" 23 .....	2	1
" 19 .....	0	0	" 24 .....	1	1
" 20 .....	2	0	" 25 .....	—	1
" 21 .....	0	1	" 26 .....	0	0
" 22 .....	0	1	" 27 .....	0	0
" 23 .....	0	0	" 28 .....	1	1
" 24 .....	2	1	" 29 .....	2	1
" 25 .....	2	2	" 30 .....	1	0
" 26 .....	2	1	May 1 .....	2	0
" 27 .....	1	2	" 2 .....	0	0
" 28 .....	1	1	" 3 .....	0	1
" 29 .....	1	2	" 4 .....	0	0
" 30 .....	0	1	" 5 .....	1	0
" 31 .....	2	0	" 6 .....	1	0
April 1 .....	—	1	" 7 .....	1	0
" 2 .....	2	0	" 8 .....	1	1

Date.	Aurora line.	Magnetic character.	Date.	Aurora line.	Magnetic character.
May 9 .....	—	1	June 20 .....	0	0
" 10 .....	2	0	" 21 .....	1	1
" 11 .....	0	0	" 22 .....	0	0
" 12 .....	0	1	" 23 .....	2	1
" 13 .....	2	2	" 24 .....	2	0
" 14 .....	2	2	" 25 .....	1	0
" 15 .....	1	2	" 26 .....	0	0
" 16 .....	—	2	" 27 .....	1	0
" 17 .....	1	1	" 28 .....	1	0
" 18 .....	0	1	" 29 .....	0	1
" 19 .....	2	2	" 30 .....	1	0
" 20 .....	1	2	July 1 .....	2	0
" 21 .....	2	0	" 2 .....	0	0
" 22 .....	1	1	" 3 .....	2	1
" 23 .....	1	0	" 4 .....	1	1
" 24 .....	2	0	" 5 .....	1	0
" 25 .....	1	0	" 6 .....	1	1
" 26 .....	0	0	" 7 .....	2	0
" 27 .....	2	1	" 8 .....	1	1
" 28 .....	2	1	" 9 .....	1	1
" 29 .....	0	0	" 10 .....	2	0
" 30 .....	1	0	" 11 .....	2	0
" 31 .....	0	0	" 12 .....	2	0
June 1 .....	2	0	" 13 .....	2	1
" 2 .....	2	0	" 14 .....	0	1
" 3 .....	0	2	" 15 .....	1	2
" 4 .....	2	1	" 16 .....	1	1
" 5 .....	1	0	" 17 .....	1	0
" 6 .....	2	0	" 18 .....	1	0
" 7 .....	—	1	" 19 .....	0	1
" 8 .....	0	2	" 20 .....	1	0
" 9 .....	1	2	" 21 .....	2	0
" 10 .....	1	1	" 22 .....	0	1
" 11 .....	1	0	" 23 .....	0	1
" 12 .....	0	0	" 24 .....	0	0
" 13 .....	1	1	" 25 .....	1	0
" 14 .....	1	1	" 26 .....	2	1
" 15 .....	1	0	" 27 .....	0	1
" 16 .....	1	0	" 28 .....	1	1
" 17 .....	2	0	" 29 .....	0	1
" 18 .....	2	0	" 30 .....	0	0
" 19 .....	1	1	" 31 .....	0	0

We have to determine whether strong aurora line is associated with strong magnetic disturbance. A first glance at the figures is not favourable to such a connection.

It is desirable to eliminate the occasion of May 13-14, when there was a very great magnetic storm, and an aurora undoubtedly of the same general character as those in the polar regions, which was seen all over Northern Europe. There is no doubt of the connection in this case, but the doubt is whether the same applies to the weak auroral light photographed on ordinary nights. It may be objected that the exclusion of these two nights is arbitrary. A definite criterion to justify it may be found in the fact that

on these occasions the nitrogen bands were stronger than the green aurora line, whereas they were not photographed at all on any other occasion. Whether justifiable or not, the omission of these two cases scarcely affects the statistical result.

If we classify the nights according to auroral intensity (excluding May 13 and 14), we get:—

Auroral intensity.....	2	1	0
Average magnetic character .....	0.49	0.67	0.53

There is here no indication whatever that high auroral intensity tends to be accompanied by magnetic disturbance.

If we classify according to magnetic character, we get:—

Magnetic character .....	2	1	0
Average auroral intensity .....	1.00	0.95	1.03

Again, there is no indication that magnetic disturbance is accompanied by strong auroral intensity.

### § 3 *Aurora Line and Sunspots.*

There is little doubt that the strong aurora of May 13-14, with accompanying magnetic storm, was connected with the great sunspot group which crossed the central meridian of the sun's discs on May 14-15, at a distance of only  $3^{\circ}$  from the centre of the disc. But for reasons already given when discussing magnetic disturbance, it is desirable to discuss separately the ordinary nights, when the photographs, if they showed anything, showed only the green aurora line, without nitrogen bands.

During the observations a daily watch was kept on the sun with a 3-inch telescope, the largest at my disposal, and the spot distribution roughly noted. There was nothing to encourage the idea of a direct connection, except in the one instance above mentioned. For instance, on the night of April 29 the aurora intensity was recorded as 2, but no spots whatever were detected on the sun on either April 28, 29 or 30.

The Astronomer Royal kindly supplied me with the times when spots of any importance crossed the central meridian of the sun from February 26 to July 31. These were fifteen in number and ranged in size from area 100 to 900, the unit being a millionth of the sun's visible hemisphere.

In order to determine if there was any tendency for the green aurora line to be strong near the time of transit of a spot across the sun's central meridian, the average auroral intensities were taken out as follows:—\*

\* When the intensity on the night of transit is referred to, the association sought is between, *e.g.*, the spot whose transit occurred on March 13 and the photographic exposure begun on the night of March 13, and finished on the morning of March 14.

Nights before transit.....	0·77
Nights of transit .....	1·15
Nights after transit .....	1·36
All nights observed .....	1·00

It will be noticed that on nights before transit the average auroral intensity was less (as it happened) than on ordinary nights. That it should be actually less is no doubt accidental, but no connection is indicated. Judging by the analogy of the auroral display of May 13-14, it is on the night before transit that the effect, if any, should be looked for. If we take the night of transit, or the night after, the line was rather more often bright than on ordinary nights. But the evidence for any connection is insufficient.

#### § 4. *Geographical Distribution.*

It is obviously important to determine how the ordinary intensity of the aurora line varies with the latitude. The natural expectation would be that it would increase to the north, when it would merge into the polar aurora. I had a convenient opportunity of making observations at Beaufront Castle, near Newcastle, and took a spectrograph there in the autumn. This instrument (No. 2) had a simple 60° prism instead of the Rutherford prism in No. 1, but otherwise the optical parts were similar. No. 2 probably gave rather the brighter spectrum if anything. The plates used were from the same box as those used at Terling before and after, thus no doubt arises about their quality.\*

Exposures of one night each were made on the following individual nights:—August 19-31 inclusive, September 6, September 27-October 8 inclusive, October 10, October 11. Quite a good proportion of these 28 nights were clear, but not one of the photographs gave a positive result. During the previous months at Terling, positive results were got on 101 nights out of a total of 145, and in no case was the result negative for more than four nights running.

This diminished intensity of the aurora line in a more northerly place was naturally accepted with reluctance, and although I did not see how the spectrograph No. 2 used at Beaufront could be less effective than No. 1 used at Terling, it was more satisfactory to test this point directly. This was done by taking the instrument No. 2 to Terling from September 20 to 26 inclusive. On six out of these seven nights the result was positive. The spectrograph was then taken back to Beaufront, and negative results obtained

\* It is my practice to cut a quarter plate into six, so that a box containing a dozen is enough for seventy-two nights.



from September 27 onwards, as already recorded. Further positive results were got with this instrument at Terling in November.

The question arose whether the aurora line was present at all in the sky at Beaufront. A cumulative exposure was made from September 1 to 5 inclusive, and showed the line strongly. Another five-night exposure, from September 7 to 11, also showed it very definitely. These cumulative exposures unavoidably interrupted the series of single night exposures at Beaufront, which have been recorded.

It emerges then very definitely, that the aurora line, though not altogether wanting, is ordinarily less bright at Beaufront than at Terling, about  $3^{\circ}$  of latitude further south. This was a very strange and unexpected result, but, on consideration, it appeared to fit in well with the results of the Californian observers  $15^{\circ}$  further to the south.

Campbell\* was able to see the aurora line whenever he looked for it. I have been quite unable to observe it visually at all at Terling, except during the display of May 13-14, though I have often looked, and have used every precaution to make the conditions favourable.

The method I prefer is to have a slit mounted in the shutter of a dark room, and to look at it through a powerful combination of direct vision prisms, which give tolerable spectroscopic purity with the slit wide. In this way, resting the eye in the dark for a time, the continuous spectrum of the night sky can be made out, and the slit may then be narrowed. I could never see the aurora line.

It may be thought inconsistent that the continuous spectrum of the night sky can be more easily *seen*, while the aurora line can be more easily *photographed*. The matter is, however, complicated by many considerations of a physiological nature, particularly the superior visibility in a bad light of an object subtending a large angle.† This favours the continuous spectrum.

Prof. Fowler informs me that he, too, has looked in vain for the aurora line on ordinary nights in the south of England. On the other hand, Prof. Michelson informs me that he has been able to see it on ordinary nights at the Yerkes Observatory (latitude  $43^{\circ}$ ).

These various experiences suggest that the aurora line is ordinarily stronger in the lower latitudes, and are thus in agreement with my results for the north compared with the south of England. I hope to carry the spectrograph further south when opportunity offers.

There is no very definite means of comparing the photographic intensities

\* 'Lick Obs. Bull.,' vol. 5, p. 46 (1908), and 'Astr. Soc. Pacific,' vol. 29, p. 218 (1917).

† See my father's observations: Rayleigh, 'Proc. Camb. Phil. Soc.,' vol. 4, p. 197 (1882); 'Scientific Papers,' vol. 2, p. 92.

I obtained with Slipher's. I have compared the Cramer plates he used with the Marion plates I used, and found them of about the same sensitiveness for yellow-green light. His instrument also appears to have been similar to mine, and he obtained the line on every plate he exposed. My experience at Terling, as described, was less favourable than this, and at Beaufront very much less favourable, so that here, too, there seems evidence that the line was stronger in California, at any rate at the time when Slipher was working. Some reserve is necessary, since these various observations were made for the most part nearer sunspot maximum than my own.

The fact that I could not detect the line at all at Beaufront in one night's exposure seems to show that auroral effects could not have interfered appreciably with the observations I made there on the colour of the night sky.\* I make this remark apropos of some criticisms when that paper was read.

#### § 5. *General Remarks.*

There seems to be no doubt of the genuine variation of the intensity of the aurora line from time to time. Generally speaking, however, if unusually strong or unusually weak, it remains so for several nights consecutively. The range of variation at one place seems not very great, but I am not prepared at present to make any numerical estimate of it. The difficulty arises partly from the varying atmospheric conditions, partly from the "inertia" of photographic plates, partly from the extreme faintness of the phenomenon itself.

The material collected suggests that the aurora line, as photographed at Terling on ordinary nights, differs not only in degree, but also in kind, from an auroral display, such as occurs frequently in the Arctic, and occasionally in temperate latitudes. There was such a display on the night of May 13 and 14, 1921, and good photographs of its spectrum were secured. These will be reproduced and discussed in a future paper. It is enough here to remark that they were entirely distinct from any other photographs of the series, the negative bands of nitrogen, and not the green line, being the predominant feature photographically. Moreover, the intensity of the green line was a large multiple of that on any other occasion.

It would be very important to determine whether the nitrogen bands are ordinarily present in the sky. An attack will be made on this problem by long exposures with a specially designed instrument.

§ 6. *Experiments Bearing on the Origin of the Green Aurora Line.*

Slipher's investigations (*loc. cit.*) gave a wave-length of 5578 for the green aurora line. This differs considerably from the old value 5570 which led some authors to identify the aurora line with krypton, and leaves little doubt that the krypton origin must be abandoned. It is, however, satisfactory to make the comparison directly, and this was frequently done in the present work, the krypton line being used for reference as already described. Many plates were obtained suitable for testing the coincidence or otherwise of the aurora line with krypton, and they all showed that krypton was the less refrangible. The photographs were not on a large enough scale to measure closer than about 3 Ångströms, but within these limits the result was consistent with Slipher's.

The auroral display of May 13-14 gave the same results, thus there is no reason to doubt that the line found in the sky on ordinary nights is really the same as the line seen in auroral displays. The consistent statement of many experienced visual observers that the (brilliant) aurora gave a wave-length of about 5570 led to some reasonable doubt on this point, for the error they made is greater than would have been supposed possible.

My colleague at the Imperial College, Prof. A. Fowler, F.R.S., has examined some of the photographs of both kind and allows me to state that he concurs that they clearly prove non-coincidence with krypton. The supposed krypton origin is, therefore, to be discarded. In any case it was obviously very difficult to imagine how so dense a gas could be concentrated in the upper atmosphere.

Although the aurora *line* is usually spoken of, it is quite possible that what we observe is the bright head of a band. It is only by the use of high resolving power that this possibility could be excluded. Since bands may be due to molecular complexes (*e.g.*, ammonia, water vapour, magnesium hydride) the field of search for a possible origin is somewhat widened by this consideration. I shall, for brevity, speak of the aurora line without intending to exclude the alternative.

In a former investigation\* it was shown that ozone must be present in the upper atmosphere, and possibly at a high concentration. This, together with the great altitude of the aurora found by Stormer† suggested that the green line might be a fluorescence spectrum of ozone, excited perhaps by the ultra-violet light of the negative nitrogen bands, which appear concurrently on the aurora.

\* 'Roy. Soc. Proc.,' A, vol. 94, p. 260 (1918).

† 'Kristiania Vid.-Selsk. Skr.,' I, M.-N.Kl. (1911), and later papers.

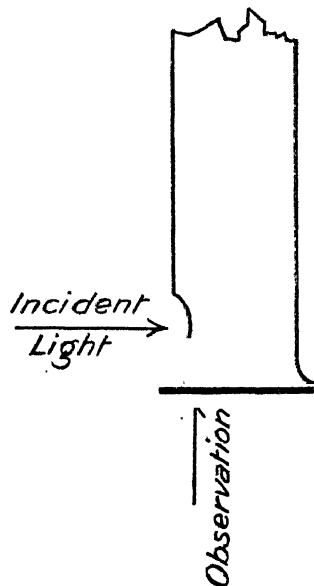
The ultra-violet light from an iron arc was separated from visible light by R. W. Wood's method of focal isolation\* using quartz lenses. This method consists, in brief, in focussing on a small hole an ultra-violet image of the source. The ultra-violet light gets through the hole, while visual light, which is not in focus is for the most part stopped.

The ultra-violet light was collected by another lens and focussed on a quartz vessel containing ozone. The ozone was prepared by Goldstein's method of vacuum discharge at low temperature.† As ultra-violet light is intensely absorbed by ozone, the fluorescent effect, if any, should be very close to the window where the light enters. The latter accordingly took the form of a dimple, sucked inwards in the quartz vessel. A clear silica window, fused on, allowed of easy observation at right angles to the incident light (see figure).

No fluorescence whatever was observed under these apparently favourable circumstances, either with the ultra-violet light from the iron arc, the entire radiation of the iron arc, visual and ultra-violet, or the cadmium spark.‡

The presence of concentrated ozone was verified after the experiment by passing an induction spark through the vessel. The ozone was decomposed with an audible click, and a bright flash passed down the tube. I looked to see if the aurora line was present in this flash. Only the sodium line could be observed, however.

The negative glow of a discharge tube containing oxygen shows a spectrum of four rather broad and more or less symmetrical bands without sharp heads. Prof. Fowler pointed out to me that the centre of the brightest of these was not far from the aurora line. It occurred to me as worth trying what would be the aspect and position of this band if produced at low temperature, such as may prevail in the auroral layer. An oxygen discharge tube was accordingly immersed in liquid air, but no tendency of the band to become narrow or to approach closer to the position of the aurora line was observed.



\* 'Physical Optics,' 1911, p. 415.

† 'Ber. Deut. Chem. Gesellsch.,' vol. 36, p. 3043 (1903).

‡ Hartley, 'J. Chem. Soc.,' vol. 63, p. 250 (1893), described a blue fluorescence of ozone illuminated by the cadmium spark. I have not succeeded in seeing this, though I had the advantage of being able to concentrate the ozone by liquefaction.

It is worth while to mention that the oxygen band is conspicuous under certain circumstances in the cathode ray spectrum of air at low pressures. It is, I believe, generally supposed that the cathode rays in air show nitrogen bands only.

I have recorded these negative results in the hope that they may suggest something more successful to a future investigator.

#### § 7. *Summary.*

(1) The spectrum of the night sky at Terling (not far from London) has been photographed systematically. The aurora line at wave-length 5578 is recorded on about two nights out of three.

(2) Its intensity on ordinary nights does not seem to be obviously related either to the amount of magnetic disturbance, or to the transit of spots over the sun's central meridian.

(3) The intensity in the neighbourhood of Newcastle is notably less than near London, thus the effect appears to increase towards the south. It would seem, therefore, to be due to some different cause from the Polar aurora.

(4) It is confirmed that the aurora line does not coincide with krypton. Some experiments to determine its origin are described, but the results are negative.

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*The Thermal Stresses in Spherical Shells Concentrically Heated.*

By CHARLES H. LEES, D.Sc., F.R.S.

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## INTRODUCTION.

1. In recent years there have been a number of failures of materials when unequally heated which appeared to be due to the stresses set up by the differences of temperature in the materials. These stresses, although unimportant for small differences of temperature and at low temperatures, may be serious for large differences at high temperatures, owing to their increase with the temperature differences and to the great reduction of the elasticities and ultimate strengths of materials at high temperatures. It is therefore desirable, when possible, to calculate the thermal stresses to which structures are liable to be subjected by the differences of temperature likely to exist in them, especially if these differences are large and the temperatures themselves high.

The circumstances producing high thermal stresses are present to an exceptional degree in metallurgical, pottery and glass furnaces, and it is in these cases that disintegration of the materials used in the construction of the furnaces is most marked. The furnaces themselves vary so much in shape and material that it is advisable at present to discuss only some simple form and material, the investigation of which presents the minimum number of mathematical difficulties.

The roughly hemispherical form of many furnaces suggests the consideration of the comparatively simple case of a concentric spherical shell concentrically heated, composed of materials for which the physical constants over the ranges of temperature considered may be taken as approximately constant.

The case of a solid sphere concentrically heated was treated by Hopkinson\* in 1879 and by Almansi† in 1897, on the assumption that, throughout the range of temperature considered, the expansion of the heated material was proportional to the rise of temperature.

It is, however, possible to cover those cases in which the differences of temperature are too great to allow this assumption to be made, by dealing in the equations connecting strain and stress directly with the expansion of the material from some standard temperature to the actual temperature,

\* Hopkinson, J., 'Mess. of Maths.,' vol. 8, p. 168 (1879):

† Almansi, 'Atti Accad. Torino,' vol. 32, p. 701 (1897).

instead of introducing the temperature and the coefficient of expansion. In the following deduction this more general method is adopted.

#### EXPANSION OF THE SHELL.

2. Let  $r$  (fig. 1) be the distance of a point from the centre of curvature of a concentric spherical shell at a uniform temperature and subjected to no stress, and let the temperature at all points of a thin shell of radius  $r$  be

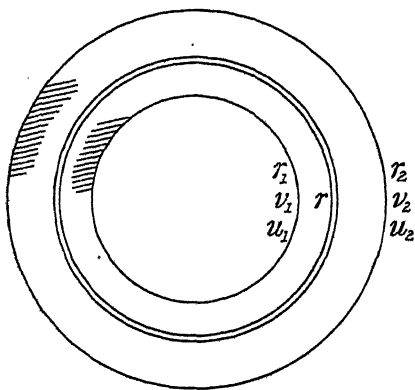


FIG. 1.—The Shell.

raised by  $\theta$ , where  $\theta$  is a function of  $r$ , and the pressure at the inside surface of the shell of radius  $r_1$  become  $R_1$ , and that at the outside surface  $r_2 = R_2$ .

If the law of linear expansion of the material of the shell is expressed by the formula  $l_\theta = l_0(1 + a\theta + b\theta^2 + c\theta^3, \text{ etc.})$ , where  $a, b, c$  are constants, we may write  $l_\theta = l_0(1 + \alpha_\theta)$ , where  $\alpha_\theta = a\theta + b\theta^2 + c\theta^3 + \text{etc.}$ , and  $\alpha_\theta$  is then the actual expansion in length of a rod initially 1 cm. long when its temperature is raised by  $\theta$ . In the same way, the change of volume may be

represented by the formula  $v_\theta = v_0(1 + \alpha_\theta)$ , where  $\alpha_\theta$  is the dilatation of 1 c.c. when its temperature is raised by  $\theta^\circ \text{C}$ .

If a thin concentric shell of internal radius  $r$  and external  $r + dr$  be removed from the main shell while at its initial temperature, have its temperature raised so that the dilatation of 1 c.c. is  $\alpha_\theta$ , its volume,  $4\pi r^2 dr$ , will be increased by  $4\pi r^2 \alpha_\theta dr$ .

If each elementary shell of the material be isolated in this way and suffer dilatation at its own special rate, the whole increase in volume of the elementary shells will be  $\int_{r_1}^{r_2} 4\pi r^2 \alpha_\theta dr$  and the mean dilatation of the

material of the shell per c.c.  $\frac{\int_{r_1}^{r_2} 4\pi r^2 \alpha_\theta dr}{\frac{4}{3}\pi(r_2^3 - r_1^3)}$ .

In general, the expanded shells would no longer fit together, and it is in forcing a fit that the stresses known as thermal stresses arise.

We note, in the first instance, that if the dilatation per cubic centimetre were the same for each shell, they would still fit together, and the thermal stresses would be zero. We therefore decompose the dilatation per cubic centimetre,  $\alpha_\theta$  of each elementary shell in the general case into two parts:

first, a part,  $\bar{\alpha}$ , equal to the mean dilatation for the whole shell; second, a part,  $\alpha_\theta'$ , equal to the excess of the actual dilatation over that mean. The first part of the dilatation introduces no stresses; the thermal stresses are all due to the second part.\*

#### THE STRESSES IN THE SHELL.

3. To find the nature and magnitude of the stresses and strains in the shell. Consider a small portion of the shell bounded by concentric spherical surfaces of radii  $r$  and  $r + dr$  respectively, and by the surface of a cone of small vertical angle with its apex at the centre of curvature of the shell (fig. 2). Let  $R$  be

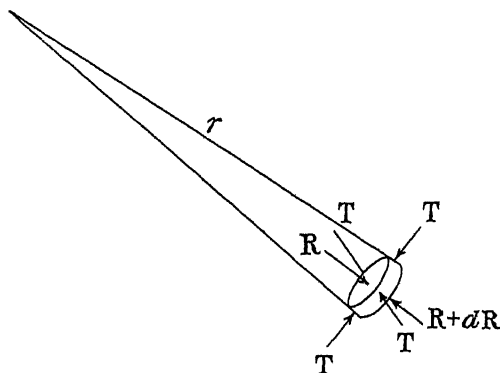


FIG. 2.—The pressures on an elementary disc.

the radial pressure on the element of the surface of the disc having radius  $r$ , and  $R + dR$  that on the surface  $r + dr$ . Let  $T$  be the tangential pressure on the conical surface of the disc. These are by symmetry the only stresses. Let  $r'$  be the radial displacement outwards from the centre of curvature of any point initially at distance  $r$  from that centre. Again by symmetry this is the only displacement.

The stress-strain equations for the elementary disc are:—

$$(1 - \sigma)T - \sigma R = -\epsilon \left( \frac{r'}{r} - \alpha_\theta' \right), \quad (3.1)$$

$$R - 2\sigma T = -\epsilon \left( \frac{dr'}{dr} - \alpha_\theta' \right), \quad (3.2)$$

where  $\epsilon$  is Young's Modulus,  $\sigma$  Poisson's ratio, supposed to be constants, and  $\alpha_\theta'$  the excess of the linear expansion of the material of the disc over the mean expansion for the whole of the shell.

\* The absence of this limitation renders the equations of Rayleigh, 'Phil. Mag.,' vol. 1, p. 170, No. 3 *et seq.* (1901); and of Love, 'Theory of Elasticity,' 2nd ed., p. 106, No. 34, too general.



The equation for equilibrium of the forces acting on the disc is

$$2Tr = \frac{d}{dr}(Rr^2). \quad (3.3)$$

Substituting the value of  $T$  from (3.3) in the former equations they become

$$(1-\sigma) \frac{1}{2r} \cdot \frac{d}{dr}(Rr^2) - \sigma R = -\epsilon \left( \frac{r'}{r} - \alpha_{\theta}' \right) \quad (3.4)$$

and 
$$R - \sigma \frac{1}{r} \frac{d}{dr}(Rr^2) = -\epsilon \left( \frac{dr'}{dr} - \alpha_{\theta}' \right). \quad (3.5)$$

Multiplying (3.4) through by  $r$ , differentiating with respect to  $r$  and adding the result to (3.5) we eliminate  $r'$  and obtain on reduction

$$r^2 \frac{d^2 R}{dr^2} + 4r \frac{dR}{dr} = \frac{2\epsilon}{1-\sigma} \cdot r \frac{d\alpha_{\theta}'}{dr} \quad (3.6)$$

the solution of which is

$$R = A + \frac{B'}{r^3} + \frac{2\epsilon}{1-\sigma} \frac{1}{r^3} \int r^2 \alpha_{\theta}' \cdot dr, \quad (3.7)$$

where  $A$  and  $B'$  are constants whose values depend on the pressures exerted on the inner and outer surfaces of the shell.

This expression for  $R$  suggests the substitution of  $v$  the volume of the shell of radius  $r$  instead of  $r$  in the equation, which becomes

$$R = A + \frac{B}{v} + \frac{2}{9} \frac{\epsilon}{1-\sigma} \cdot \frac{1}{v} \int^v \alpha_{\theta}' \cdot dv,$$

or 
$$Rv = Av + B + \frac{2}{9} \frac{\epsilon}{1-\sigma} \int^v \alpha_{\theta}' dv. \quad (3.8)$$

If  $R_1$  is the pressure on the inner surface  $r_1$  of volume  $v_1$ , and  $R_2$  that on the outer  $r_2$  of volume  $v_2$  we have

$$R_1 v_1 = A v_1 + B + \frac{2}{9} \frac{\epsilon}{1-\sigma} \int_{v_1}^{v_1} \alpha_{\theta}' \cdot dv$$

and 
$$R_2 v_2 = A v_2 + B + \frac{2}{9} \frac{\epsilon}{1-\sigma} \int_{v_1}^{v_2} \alpha_{\theta}' dv.$$

On eliminating  $A$  and  $B$  from these equations and reducing we have

$$R = R_2 + (R_1 - R_2) \frac{v_2/v - 1}{v_2/v_1 - 1} - \frac{2}{9} \cdot \frac{\epsilon}{1-\sigma} \cdot \frac{1}{v} \int_v^{v_2} \alpha_{\theta}' dv,$$

writing  $E'$  for the expansion  $\int_{v_1}^v \alpha_{\theta}' dv = - \int_v^{v_2} \alpha_{\theta}' dv$ , due to the rise of temperature of that part of the shell within the spherical surface of volume  $v$  we have

$$R = R_2 + (R_1 - R_2) \frac{v_2/v - 1}{v_2/v_1 - 1} + \frac{1}{9} \frac{\epsilon}{1-\sigma} \cdot 2 \frac{E'}{v}, \quad (3.9)$$

or if  $u = 1/v$

$$R = \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} + (R_1 - R_2) \frac{u}{u_1 - u_2} + \frac{1}{9} \frac{\epsilon}{1 - \sigma} \cdot 2u E'. \quad (3.9')$$

To determine  $T$  we have from equation (3.3)  $T = R + \frac{r}{2} \frac{dR}{dr}$ , and on introducing the volume  $v$  instead of the radius  $r$ ,

$$T = R + \frac{3}{2} v \frac{dR}{dv}. \quad (3.10)$$

On substituting the values of  $R$  and  $dR/dv$  in this equation and reducing we get

$$T = R_2 - (R_1 - R_2) \frac{v_2/2v + 1}{v_2/v_1 - 1} + \frac{1}{9} \frac{\epsilon}{1 - \sigma} \left( 3\alpha_\theta' - \frac{E'}{v} \right), \quad (3.11)$$

or in terms of  $u$

$$T = \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} - \frac{R_1 - R_2}{2} \frac{u}{u_1 - u_2} + \frac{1}{9} \frac{\epsilon}{1 - \sigma} (3\alpha_\theta' - uE'). \quad (3.11')$$

The "mean pressure" or "equivalent hydrostatic pressure" to which the material of the shell at any point is subjected is  $(R + 2T)/3$  and the preceding equations give us

$$\frac{R + 2T}{3} = \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} + \frac{1}{9} \frac{\epsilon}{1 - \sigma} \cdot 2\alpha_\theta'. \quad (3.12)$$

The two shear stresses in diametral planes at right angles to each other are  $(R - T)/3$  and our equations give

$$\frac{R - T}{3} = \frac{R_1 - R_2}{2} \cdot \frac{u}{u_1 - u_2} - \frac{1}{9} \frac{\epsilon}{1 - \sigma} (\alpha_\theta' - uE'). \quad (3.13)$$

Writing  $v'$  for the increment of volume  $v$  of the spherical surface of radius  $r$  owing to the displacement  $r'$ , and  $u'$  for the increment of  $u = 1/v$ , we have since  $\frac{r'}{r} = \frac{1}{3} \frac{v'}{v} = -\frac{1}{3} \frac{u'}{u}$ , on substituting the values of  $R$  and  $T$  in equation (3.1) and rearranging

$$\begin{aligned} \frac{r'}{r} = \frac{1}{3} \frac{v'}{v} = -\frac{1}{3} \frac{u'}{u} = -\frac{1 - 2\sigma}{\epsilon} \cdot \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} \\ + \frac{1 + \sigma}{\epsilon} \cdot \frac{R_1 - R_2}{2} \frac{u}{u_1 - u_2} + \frac{1}{9} \frac{1 + \sigma}{1 - \sigma} \cdot \frac{E'}{v} \end{aligned} \quad (3.14)$$

It may be noted that

$$\frac{1 - 2\sigma}{\epsilon} = \frac{1}{3k} \quad \text{and} \quad \frac{1 + \sigma}{\epsilon} = \frac{1}{2\mu},$$

where  $k$  is the bulk modulus and  $\mu$  the rigidity of the material.

The connection between  $r'/r$  and  $R$  is obtained readily by eliminating  $T$  and  $\alpha_\theta'$  from the original equations which gives  $\frac{d}{dr} \left( \frac{r'}{r} \right) = \frac{1 + \sigma}{2\epsilon} \frac{dR}{dr}$ . (3.15)

The stresses and displacements due to the internal and external pressures  $R_1$  and  $R_2$  agree with Lamé's results.\*

On putting  $r_1 = 0$ ,  $R_1 = R_2 = 0$  and  $\alpha_\theta' = 3a\theta'$  in these equations, the thermal stresses reduce to Hopkinson's values for a solid sphere in which the range of temperature is small enough to allow the expansion with rise of temperature to be taken as uniform.

4. From these expressions it is seen that the cubical compression due to the pressures  $R_1$  and  $R_2$  on the surfaces of the shell is the same throughout the material,† while that due to the temperature distribution is at any point proportional to the excess of the thermal dilatation at that point over the mean thermal dilatation of the whole material of the shell.

The radial pressure  $R$ , the displacement  $r'/r$ , the tangential pressure  $T$ , and the shear stresses in diametral planes at right angles to each other, due to the pressures on the surfaces, are all linear functions of  $u$  the reciprocal of the volume  $v$  of the sphere through the point. The radial pressure  $R$ , and the displacement  $r'/r$ , due to the temperature distribution are proportional to the quotient of the excess cubical expansion of the elementary shells between the inner surface  $v_1$  and the surface  $v$ , by the volume  $v$  of the latter surface. The other thermal stresses are found by the usual combinations of radial pressure and the mean pressure.

We see from the foregoing investigation that the general problem of the stresses in a spherical shell, produced by change of temperature such that isothermal surfaces are concentric spheres and by pressures applied to its surfaces, resolves itself into the determination by the methods indicated above of the stresses and displacements due to the expansion  $\alpha_\theta'$  of each elementary shell above or below the mean  $\bar{\alpha}$  for the whole shell, and the superposition on these of the displacements due to the mean expansion  $\bar{\alpha}$  and of the stresses and displacements due to the pressures  $R_1$  and  $R_2$  applied to the inner and outer surfaces of the expanded shell.

#### GRAPHICAL REPRESENTATION OF STRESSES.

5. It is not easy to realise the meanings of the foregoing expressions for the stresses due to mechanical and to thermal causes without graphic representation and the expressions themselves suggest the following method of representing the stresses at a point,  $r$ , in terms of the volume,  $v$ , of the sphere through the point, or in the first case in terms of the reciprocal,  $u$ , of that volume.

\* See e.g., Love, 'Theory of Elasticity,' 2nd ed., pp. 139, 140 (1906).

† The constancy of the cubic compression due to the pressures on the two surfaces is noted by Lamb in his 'Statics,' p. 332 (1912).

## A. Stresses due to Pressures on Inside and Outside Surfaces.

Set off along the axis of abscissæ (fig. 3) the reciprocals  $OU_1 = u_1$  and  $OU = u_2$  of the volumes  $v_1$  and  $v_2$  of inside and outside surfaces. At  $U_2$  erect an ordinate,  $U_2R_2$ , equal on some convenient scale to the pressure,  $R_2$ , on the outside surface. Join the top,  $R_2$ , of this ordinate to the point  $U_1$  and produce to cut the pressure axis in  $S_0$ . Through  $S_0$  draw a line parallel to the axis of abscissæ, and let it cut the ordinates through  $U_1$  and  $U_2$  in  $S_1$  and  $S_2$ .

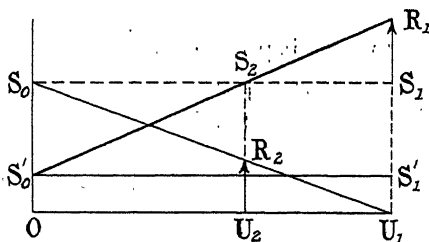


FIG. 3.—The mean pressure  $OS_0'$  determined by  $U_2R_2$ ,  $U_1R_2S_0$ ,  $S_0S_1$ ,  $S_1R_2$ , and  $R_1S_2S_0'$ .

Set off above  $S_1$  a length,  $S_1R_1$ , equal to  $R_1$ , the pressure on the inside surface, and join the end,  $R_1$ , of this ordinate to  $S_2$ , and produce to cut the axis of pressures in  $S_0'$ .

Then  $OS_0$  is  $R_2 \frac{u_1}{u_1 - u_2}$ ,  $S_0S_0'$  is  $R_1 \frac{u_2}{u_1 - u_2}$ : hence

$$OS_0' = \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2}, \quad (5.1)$$

that is the "mean pressure" or "mean hydrostatic pressure" throughout the shell.

To get the terms involving  $(R_1 - R_2) \frac{u}{u_1 - u_2}$  necessary to express the various stresses, erect at  $U_1$ , fig. 4, the ordinate  $U_1A = (R_1 - R_2)$ , join the

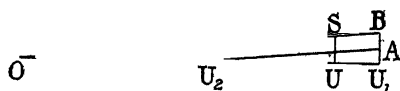


FIG. 4.— $U_1A = R_1 - R_2$ ,  $OB$  is parallel to  $U_2A$ ,  $US$  gives the stress at  $U$ .

extremity  $A$  of it to the point  $U_2$  and draw through  $O$  a straight line  $OB$ , parallel to this join, cutting  $U_1A$  in  $B$ . The ordinate  $US$  at any point  $U$  is then  $(R_1 - R_2) \cdot \frac{u}{u_1 - u_2}$ . Hence the sheer stress in each of two mutually perpendicular diametral planes through the point  $U$

$$= \frac{1}{2} \cdot US. \quad (5.2)$$

For the other stresses we have

$$R = \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} + (R_1 - R_2) \frac{u}{u_1 - u_2} = OS_0' + US, \quad (5.3)$$

$$T = \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} - \frac{R_1 - R_2}{2} \frac{u}{u_1 - u_2} = OS_0' - \frac{1}{2} US, \quad (5.4)$$

and for the displacements

$$\left. \begin{aligned} \frac{r'}{r} = \frac{1}{3} \frac{v'}{v} &= -\frac{1-2\sigma}{\epsilon} \frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} + \frac{1+\sigma}{\epsilon} \frac{R_1 - R_2}{2} \frac{u}{u_1 - u_2} \\ &= -\frac{1-2\sigma}{\epsilon} OS_0' + \frac{1+\sigma}{\epsilon} \frac{1}{2} US \end{aligned} \right\} \quad (5.5)$$

### B. Stresses due to the Deviation of the Dilatation due to Temperature from the mean Dilatation.

6. Set off (fig. 5) as abscissæ  $OV_1, OV_2$ , the volumes,  $v_1$  and  $v_2$  of the inner and outer surfaces of the shell. Take as ordinates the values of  $E'$ , the increase of volume of the series of infinitely thin shells between  $v_1$  and  $v$  due to the excess of the temperature of each shell over the mean temperature of the whole of the shells between the inner and outer surfaces.

We thus get the curve of volume increase,  $V_1, PV_2$ , extending from  $V_1$ ,

where it cuts the axis of volumes, to  $V_2$ , where it again cuts the axis. As we proceed outwards it slopes upwards, where the layers are hotter, or the dilatations greater, than the mean, and downwards, where they are colder, or where the dilatation is below the mean. The slope upwards at any point is proportional to the excess dilatation per cubic centimetre on the scale taken.

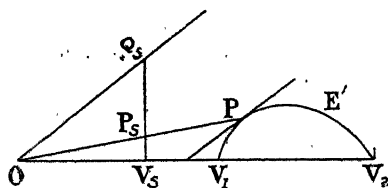


FIG. 5.— $E'$  the excess expansion curve gives at P with  $OQ_s$  parallel to the tangent at P, the lines  $V_s P_s, V_t Q_s$  determining the stresses.

Join P, a point on the curve, to the origin, O. Through O draw  $OQ_s$  parallel to the tangent to the  $E'$  curve at P, and at  $V_s$ , corresponding to a volume  $v_s$ , a convenient multiple of 10, erect a perpendicular to the volume axis, cutting  $OQ_s$  in  $Q_s$  and OP in  $P_s$ .

Then the radial pressure R at the point P is

$$\frac{1}{9} \frac{\epsilon}{1-\sigma} \cdot 2 \frac{V_s P_s}{v_s}, \quad (6.1)$$

the "mean pressure" at P is

$$\frac{1}{9} \frac{\epsilon}{1-\sigma} \cdot 2 \frac{V_s Q_s}{v_s}, \quad (6.2)$$

the tangential pressure  $T$  is

$$\frac{1}{9} \frac{\epsilon}{1-\sigma} \frac{3V_s Q_s - V_s P_s}{v_s}, \quad (6.3)$$

the two shear stresses are

$$-\frac{1}{9} \frac{\epsilon}{1-\sigma} \cdot \frac{P_s Q_s}{v_s}, \quad (6.4)$$

and the radial displacement is given by

$$\frac{r'}{r} = \frac{1}{3} \frac{v'}{v} = \frac{1}{9} \frac{1+\sigma}{1-\sigma} \cdot \frac{V_s P_s}{v_s}. \quad (6.5)$$

To the latter must be added in case the mean temperature has been raised  $\bar{\theta}$  the radial displacement given by  $\frac{r'}{r} = \bar{\alpha} = \frac{1}{3} \bar{\alpha}$  due to it.

#### CONSTRUCTION OF THE EXCESS EXPANSION CURVE $E'$ .

7. The problem of determining the thermal stresses at a point in the material of the shell thus reduces to the construction of the curve  $E'$ , and the drawing of the radius vector and tangent to the curve at the point.

To draw the curve most conveniently we have  $E' = \int_{v_1}^v \alpha_\theta' dv$ , where  $\alpha_\theta'$  is the excess of the cubical dilatation of 1 c.c. at  $\theta$ , over the mean dilatation  $\bar{\alpha}$  for the whole shell.

Hence if  $\alpha_\theta$  is the actual dilatation at  $\theta$ ,

$$E' = \int_{v_1}^v (\alpha - \bar{\alpha}) dv = \int_{v_1}^v \alpha_\theta dv - \bar{\alpha} (v - v_1),$$

$$\text{or if} \quad E = \int_{v_1}^v \alpha_\theta \cdot dv \quad \text{and} \quad E_2 = \int_{v_1}^{v_2} \alpha_\theta \cdot dv = \bar{\alpha} (v_2 - v_1),$$

$$E' = E - E_2 \frac{v - v_1}{v_2 - v_1}. \quad (7.1)$$

We, therefore, proceed as follows:—Draw first the curve of temperature distribution,  $\theta$  (fig. 6), throughout the shell as determined by the temperatures at the two surfaces and the laws of conductivity.

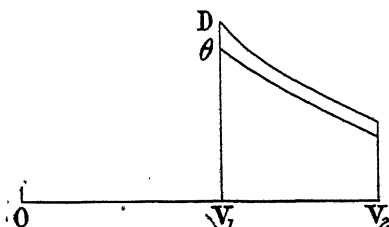


FIG. 6.

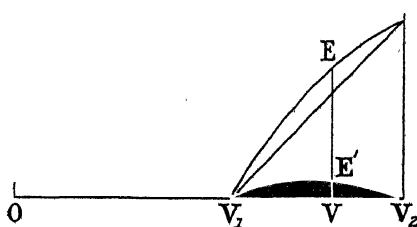


FIG. 7.

FIG. 6.— $\theta$  the curve of temperature,  $D$  the curve of dilatation.

FIG. 7.—The excess expansion curve  $E'$  obtained from the expansion curve  $E$ .

For each temperature estimate from tables of the expansion of the material of the shell the dilatation,  $\alpha_\theta$ , of 1 c.c. at each part of the shell, and draw the curve of dilatation per cubic centimetre,  $D$ , to correspond to the temperature curve. Find the total expansion,  $E$ , that is the area included between the axis of volume, the  $D$  curve, the ordinate through  $v_1$  and that through  $v$  for different values of  $v$  up to  $v_2$ , and plot the values in terms of  $v$ , curve  $E$  (fig. 7).

Join the end of the curve at  $v_2$  with its starting point at  $v_1$ . The excess of the ordinate of the curve at any point over the ordinate of the join is the ordinate of the excess cubical expansion curve,  $E'$ , required.

#### DEDUCTIONS FROM THE EXCESS EXPANSION CURVE.

8. The curves of excess cubical expansion,  $E'$  in terms of  $v$  allow the conditions for zero and maximum values of the various stresses to be seen by inspection in many cases. If the dilatation due to temperature decreases as we proceed outwards through the shell, the curve  $E'$  will have one maximum between its zeros at  $v_1$  and  $v_2$ , while if the temperature and dilatation increase outwards  $E'$  will have one minimum between its zeros. If the dilatation is a maximum at some layer within the shell the curve,  $E'$ , on starting from its zero at  $v_1$ , is first negative, then passes through zero and becomes positive and ends at zero at  $v_2$ . If the dilatation is a minimum at a layer within the shell, the curve starts by being positive near its  $v_1$  zero, passes through zero and becomes negative before reaching its  $v_2$  zero.

In all cases the maximum and minimum ordinates of the  $E'$  curve occur at the layers for which the dilatation due to temperature has the mean value for the whole shell. The ordinate is a maximum if the dilatation decreases outwards and a minimum if it increases.

The displacement is zero for points at which the  $E'$  curve crosses the axis of volumes. Two of these points are at the inner and outer surfaces respectively. The maximum outwards displacement occurs at the layer for which the tangent to the  $E'$  curve where it is positive passes through the origin, and the maximum inwards displacement at the layer for which the tangent to the curve where it is negative passes through the origin. Both layers are nearer to the centre of the sphere than the layers of maximum or minimum  $E'$ .

The radial pressure is also zero at points at which the  $E'$  curve crosses the axis. Two of the points are at the inner and outer surfaces respectively. The maximum value of the radial pressure occurs in the same layer as the maximum outward displacement, and the maximum radial tension in the layer of maximum inward displacement. These layers are a little nearer the

centre of the sphere than those of maximum and minimum ordinates of the  $E'$  curve respectively.

The mean pressure about a point vanishes at the layers for which the dilatation is the mean for the whole shell, that is at the maximum  $E'$ . The maximum values of the mean pressure occur in the layers for which the temperature dilatation differs most from the mean, that is, where the slope of the  $E'$  curve is greatest. In most practical cases this will be at or near the inner and outer surfaces and at the layer within at maximum or minimum temperature if such exists. The mean pressure is positive in the hotter and negative (*i.e.*, a tension) in the cooler portions of the shell.

The two shears in diametral planes at right angles to each other are zero for the layers for which the tangent to the  $E'$  curve passes through the origin, that is for the layers for which the displacements and the radial pressures are numerically greatest. They are greatest when the temperature dilatation is above the mean and is increasing outwards, or when it is below the mean and is decreasing outwards.

The tangential pressure is zero in a layer between that of mean dilatation and that of maximum radial pressure, for which the slope of the  $E'$  curve is one-third that of the join of the point on the curve with the origin. In general the tangential pressure is positive and large at or near the layer at highest temperature, and negative (*i.e.*, a tension) and large at or near that at lowest temperature.

From the foregoing it is seen that the determination of the stresses produced in a spherical shell by differences of temperature concentric with the shell is reduced to that of calculating the expansions of the elementary layers of the shell due to the deviation of their temperature from the mean temperature of the whole shell.

#### THE TEMPERATURE DISTRIBUTION.

9. The determination of the distribution of temperature throughout the shell, given the temperatures of the two surfaces, is a problem in heat or temperature conductivity, which if the conductivity of the material were independent of the temperature, could be solved by the usual methods. If the thermal conductivity,  $k$ , of the material cannot be taken as independent of the temperature the condition for continuity of flow of heat in the material must be given the general form

$$c\rho \frac{\partial \theta}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( kr^2 \frac{\partial \theta}{\partial r} \right), \quad (9.1)$$

where  $c$  is the specific heat and  $\rho$  the density of the material.

The difficulty of determining  $\theta$  as a function of the time and radius by



means of this equation, when  $c$  and  $k$  both vary considerably with temperature, is sufficient justification for making some simplifying assumptions in order to obtain some idea of the magnitudes of the thermal stresses in materials under common practical conditions.

#### THE STEADY STATE.

10. In the first instance let us assume that the temperature at each point of the material has become steady. Our equation reduces to  $\frac{d}{dr} \left( kr^2 \frac{d\theta}{dr} \right) = 0$ , which on integration gives

$$k \frac{d\theta}{dr} = -\frac{H}{4\pi r^2}, \quad (10.1)$$

where  $H$  is the heat which flows outward through the shell per second.

The heat conductivity  $k$  in general decreases with increase of temperature,\* but there appear to be some furnace materials for which it is approximately independent of temperature.†

Assuming that the shell is of such a material, we have for the temperature

$$\theta = A + \frac{H}{4\pi kr}.$$

If the volume  $v_2 - v_1$  of the material of the shell is small compared to its internal volume  $v_1$  this may be given the approximate form

$$\frac{\theta - \theta_2}{\theta_1 - \theta_2} = \frac{v_2 - v}{v_2 - v_1}, \quad (10.2)$$

where as before,  $\theta_1$  and  $\theta_2$  are the temperatures at the surfaces and the mean temperature  $\bar{\theta} = \frac{\theta_1 + \theta_2}{2}$ .

Taking the expansion of the material of the shell to be proportional to the excess of temperature over the mean, this gives for the expansion,  $E'$ , of the elementary shells between the inner surface,  $v_1$ , and that of volume  $v$ ,

$$E' = \frac{\alpha}{2} \cdot \frac{\theta_1 - \theta_2}{v_2 - v_1} \cdot \left\{ \left( \frac{v_2 - v_1}{2} \right)^2 - \left( \frac{v_2 + v_1}{2} - v \right)^2 \right\}. \quad (10.3)$$

The maximum value of  $E'$  is  $\frac{\alpha}{2} (\theta_1 - \theta_2) \frac{v_2 - v_1}{4}$  and occurs at  $v = \frac{v_2 + v_1}{2}$ .

The maximum  $R$  is approximately

$$\frac{1}{9} \frac{\epsilon}{1 - \sigma} \cdot \frac{\alpha}{2} (\theta_1 - \theta_2) \frac{v_2 - v_1}{v_2 + v_1}, \quad (10.4)$$

\* Lees, 'Phil. Trans. Roy. Soc.,' A, vol. 191, p. 399 (1896); Eucken, 'Ann. der Phys.,' vol. 34, pp. 217, 219 (1911).

† Clement and Egly, 'Univ. of Illinois Bulletin,' vol. 6, No. 42 (1909).

and occurs slightly within the middle layer of the shell. It is a pressure if  $\theta_1 > \theta_2$  and a tension if  $\theta_1 < \theta_2$ .

The maximum  $T$  is approximately

$$\frac{1}{9} \frac{\epsilon}{1-\sigma} \cdot \frac{3\alpha}{2} (\theta_1 - \theta_2), \quad (10.5)$$

and is found at the surfaces. At the inside it is a pressure, at the outside surface a tension if  $\theta_1 > \theta_2$ .

The maximum value of the mean pressure about a point is

$$\frac{1}{9} \frac{\epsilon}{1-\sigma} \cdot \alpha (\theta_1 - \theta_2), \quad (10.6)$$

and occurs at the surfaces.

The maximum shears are

$$\frac{1}{9} \frac{\epsilon}{1-\sigma} \cdot \frac{\alpha}{2} (\theta_1 - \theta_2) \quad (10.7)$$

at the surfaces.

The maximum displacement is

$$\frac{1}{9} \frac{1+\sigma}{1-\sigma} \cdot \frac{\alpha}{4} (\theta_1 - \theta_2) \frac{v_2 - v_1}{v_2 + v_1}, \quad (10.8)$$

and occurs approximately at the middle layer of the shell.

#### NUMERICAL VALUES : PRACTICAL STEADY CASE.

11. When we attempt to assign numerical values to these quantities in any practical case, we are met by the difficulty that we have little or no knowledge of the expansion of the materials of furnaces at high temperature, and no knowledge whatever of their elastic constants and ultimate strengths at high temperatures.

If the wall of the furnace is 20 cm. thick, and the temperature inside is  $1100^\circ \text{C.}$ , and outside  $100^\circ \text{C.}$   $\theta_1 - \theta_2$  is  $1000^\circ \text{C.}$ , and, if we take the wall to be of material of about the physical properties of firebrick at ordinary temperatures, we should have the coefficient of cubical expansion  $12 \times 10^{-6}$ , Young's modulus about  $3 \times 10^{11}$ , Poisson's ratio about  $1/3$ , a crushing strength of about  $5 \times 10^8$ , and a tensile strength of about  $2 \times 10^8$  dynes per square centimetre.\* At higher temperatures the expansion is greater, Young's modulus less, the crushing strength less, and the tensile strength probably considerably less than at ordinary temperatures.

Calculating the stresses on the basis of the above figures we have for the maximum :—

$$\text{Radial pressure } R = 3 \times 10^8 \cdot \frac{v_2 - v_1}{v_2 + v_1} \text{ near the middle of the wall.}$$

\* From Mark's 'Mechanical Engineer's Handbook.'

Tangential pressure  $T = 3 \times 10^8$ , positive at the inside surface and negative, that is a tension, at the outside surface.

Mean pressure at a point  $= 2 \times 10^8$ , positive at the inside, negative at the outside surface.

Shear stress  $= 1.0 \times 10^8$  at the surfaces.

Displacement  $= 0.7 \times 10^{-3} \frac{v_2 - v_1}{v_2 + v_1}$  near the middle of the wall.

\* These maxima exceed the limits of tensile strength of the material, and cracks would be formed on the outer surface, even if the wall were solid. If the bricks were set in cement, the cracks would form at the joints.

#### UNSTEADY STATES.

12. If the temperature throughout the shell is not steady, the  $E'$  curves are much more complicated in shape, and some of the stresses may be considerably greater than they are in the steady state.

Suppose, for example, that the shell is all at  $100^\circ \text{C.}$  and the inner surface is suddenly raised to  $1100^\circ \text{C.}$  After the first few seconds, the  $E'$  curve, corresponding to the temperature distribution, starts from the  $v_1$  zero at an angle to the axis of volume whose tangent is double that for the steady state. The maximum ordinate of the curve is, however, much smaller than in the steady state, and the inclination of the curve to the axis of volume at the  $v_2$  zero is also much smaller. Hence the tangential pressure,  $T$ , the shear stresses, and the mean pressure at the inner surface, are approximately double those in the steady state at the inner surface, and the tangential tension at the outer surface smaller than that in the steady state. The radial pressure,  $R$ , and the radial displacement do not exceed the values attained in the steady state.

As a second case, suppose the shell, after attaining the steady state with inside temperature  $1100^\circ \text{C.}$  and outside  $100^\circ \text{C.}$ , has its inside surface suddenly cooled to  $100^\circ \text{C.}$  The  $E'$  curve at a second or two after the change proceeds from the inner  $V_1$  zero, with a downward slope equal to the upward slope in the steady state. The tangential pressure at the inner surface in the steady state becomes an equal tangential tension, the mean pressure and the shear stresses are reversed, while the maximum radial pressure and the displacement retain approximately the values they had in the steady state. At the outer surface the stresses change from their steady values slowly.

Thus a sudden rise of the temperature of the inside of the shell from its initial value, supposed to be that of the outside surface, introduces at the inner surface double the tangential pressure, the mean pressure and the

shear stresses which exist at that surface in the steady state, hence spalling may result.

A sudden fall of the inside temperature from that of the steady state to that of the outside surface converts the tangential pressure of the steady state at that surface into an equal tension, the mean pressure into an equal tension, and reverses the sign of the shear stress.

Although the tangential pressure at the inner surface in the steady state may not have been sufficient to cause crushing, the tension thus produced may cause radial cracks, owing to the tensile strength of the material being less than its crushing strength.

#### FURNACES.

13. Through the kindness of Sir Robert Hadfield and of Dr. J. W. Mellor I have been able to inspect furnaces which have been in use for some time and to examine fractured materials, and the appearances of the cracks in the bricks or other materials of the furnaces show that the above theory reproduces the principal facts. The general tendency of rapid internal heating to produce spalling of the inner surface, and of rapid cooling to produce radial cracks, is quite well known to those in charge of the furnaces, and proper steps are taken to reduce the rate of change of temperature when the furnace has to be heated or cooled. A furnace which is to be taken down or repaired is cooled rapidly by blowing cold air through it in order to produce disintegration of the walls and facilitate the taking-down process.

#### CONCLUSION.

14. It is thus evident that the stresses in the wall of a furnace of spherical or approximately spherical form produced by a distribution of temperature throughout the wall, which is either known from observation or calculable by the laws of conduction of heat, can be determined readily by graphical or other methods if the law of expansion of the material throughout the range of temperature is known, and Young's modulus and Poisson's ratio or any two elastic moduli are also known, and can be taken as approximately constant. Whether the stresses thus determined will produce crushing or rupture of the wall depends on the values of the crushing load or the tensile strength of the material at the temperature which exists in the region of the stress. But the forms of the expressions for the stresses show that these stresses are proportional to the product of the dilatation of the material with rise of temperature into Young's modulus for the material. In seeking better refractory materials for furnace walls, we require to keep this product as low as possible. A low Young's modulus generally

means a correspondingly low tensile strength, but if a material could be found with a lower modulus, and a strength not reduced, it would, other things being equal, be superior. The search for a material with a low dilatation with rise of temperature seems more promising, and it is probably on account of its low dilatation that silica brick has proved so useful in furnace construction.

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*The Two-dimensional Slow Motion of Viscous Fluids.*

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(Received June 30, 1921.)

The present paper is a contribution to the treatment of problems which require a solution of the differential equation  $\nabla^4\psi = 0$ . Amongst such problems are to be found not only the very slow motions of a viscous fluid in two dimensions, but also the flexure of thin flat plates.\*

The prosecution of the investigation has been made possible by the support of the Department of Scientific and Industrial Research, which has provided financial assistance to enable two of us to devote the whole of our time to the research, and our thanks are offered to the Department for its assistance. We also desire to acknowledge the facilities afforded by the Governing Body of the Imperial College of Science and Technology in placing a room at our disposal in the Department of Aeronautics.

The method of attack was suggested by the results of an earlier paper† on the solution of Laplace's equation,  $\nabla^2\psi = 0$ . It was there found that, for any forms of single or double boundary, the solution of problems on the torsion of cylinders or the irrotational motion of an inviscid fluid could be made to depend on a number of definite integrals. In general, the evaluation of these integrals involves the use of graphical and mechanical methods, and much progress has been made in the direction of simplification of the processes. It is hoped that a paper may be presented elsewhere in the near future showing the application to a number of engineering problems.

The solution of the equation  $\nabla^4\psi = 0$  given in the present paper follows the earlier work in its generality as to boundary forms and also in the general dependence on graphical and mechanical integration for arithmetical

\* Lamb, 'Hydrodynamics,' p. 604.

† 'Roy. Soc. Proc.' A, vol. 95, pp. 457-475 (1919).

results. It happens, however, that the sample chosen for illustration, the flow of a viscous fluid past a circular cylinder in a parallel-walled channel, admits of the use of purely analytical methods for the greater part of the work. It has been found possible to give an approximate expression for the stream function  $\psi$  in analytical form, and the stream-lines illustrated in fig. 6 were obtained from the formula given on page 409 (equation 57).

*Method of Solution.*

Denoting by  $\nabla^2$  the differential operator  $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$  the solution of the equation

$$\nabla^4 \psi = 0 \quad (1)$$

is required for certain boundary conditions. In the case of slow motion in a viscous fluid such boundary conditions are given in the form

$$\left. \begin{array}{l} \psi \text{ constant on any solid boundary} \\ \partial \psi / \partial n \text{ zero on any solid boundary} \end{array} \right\} \quad (2)$$

and  
These conditions are the mathematical expression of the physical idea that there is no relative motion between a solid and the fluid in contact with it. The validity of these boundary conditions has received very strong support from recent experiments by Dr. T. E. Stanton, F.R.S.,\* in which velocities have been measured in pipes at very small distances from the walls, and even in the case of violently unsteady motion there is no indication of any failure of the equations as now understood to account for observed motion with the boundary conditions of no slipping. A critical discussion of earlier experiments is to be found in the standard treatises dealing with fluid motion.†

If, following normal usage, we write

$$\zeta \equiv \nabla^2 \psi \quad (3)$$

the differential equation (1) becomes

$$\nabla^2 \zeta = 0, \quad (4)$$

but the boundary conditions are not in a form suitable for a solution of (4) by the methods of the paper dealing with Laplace's equation. From the ideas there developed, however, we adopt that which says that a solution of (4) may be obtained in terms of the boundary values of  $\zeta$ , and that a certain distribution of simple sources on the boundary can be found which satisfies the conditions of the problem. For reasons connected wholly with the

\* 'Phil. Trans.,' A, vol. 214, p. 199 (1913).

† Lamb, 'Hydrodynamics,' p. 571.



In one of the forms used in the theory of attractions, Green's theorem states that

$$2\pi\psi_M = \iint \zeta_P \log PM \, dx_P \, dy_P + \int \psi_F \, d\theta_{FM} - \int \frac{\partial\psi}{\partial n_F} \log FM \, ds_F \quad (7)$$

where the line integrals in question are to be taken round the boundary. In this equation it may be noted that the two line integrals are immediately calculable from the boundary conditions appropriate to viscous fluid motion, and that the only undetermined quantity when M is on the boundary is  $\zeta_P$ . Equation (7) is then an integral equation for the finding of  $\zeta_P$  from the known boundary conditions.

Using the value of  $\zeta_P$  given by (6) in (7) leads to a modified result in terms of boundary doublets  $d\chi_Q$ ; in the process of substitution, however, a change in the order of integration has been made to obtain

$$2\pi\psi_M = \int \left\{ \iint \frac{\sin \gamma_{QP}}{QP} \log PM \, dx_P \, dy_P \right\} d\chi_Q + \int \psi_F \, d\theta_{FM} - \int \frac{\partial\psi}{\partial n_F} \log FM \, ds_F. \quad (8)$$

The value of  $\iint \frac{\sin \gamma_{QP}}{QP} \log PM \, dx_P \, dy_P$  depends only on the geometry of the boundary and the positions of the points Q and M, and may therefore be determined in any case without prior knowledge of the distribution of doublets appropriate to the physical problem. By a second use of Green's theorem, this evaluation is made to depend on single integrals, for

$$2\pi \cdot QM \cdot \log QM \cdot \sin \gamma_{QM} = 2 \iint \frac{\sin \gamma_{QP}}{QP} \cdot \log PM \cdot dx_P \, dy_P \\ + \int QF \cdot \log QF \cdot \sin \gamma_{QF} \, d\theta_{FM} - \int \frac{\partial}{\partial n_F} (QF \cdot \log QF \cdot \sin \gamma_{QF}) \cdot \log FM \cdot ds_F \quad (9)$$

is generally true for the conditions for which Green's theorem is valid.

Combining equations (8) and (9) so as to eliminate the double integral of the latter leads to

$$2\pi\psi_M = \int \left\{ \pi \cdot QM \cdot \log QM \cdot \sin \gamma_{QM} - \frac{1}{2} \int QF \cdot \log QF \cdot \sin \gamma_{QF} \, d\theta_{FM} \right. \\ \left. + \frac{1}{2} \int \frac{\partial}{\partial n_F} (QF \cdot \log QF \cdot \sin \gamma_{QF}) \log FM \cdot ds_F \right\} d\chi_Q \\ + \int \psi_F \, d\theta_{FM} - \int \frac{\partial\psi}{\partial n_F} \cdot \log FM \, ds_F. \quad (10)$$



It is convenient for further analysis that the differentiation normal to the boundary be performed generally (see fig. 2).

$$\begin{aligned}\frac{\partial \gamma_{QF}}{\partial n_F} &= \frac{\sin \gamma_{FQ}}{QF}, & \frac{\partial \cdot QF}{\partial n_F} &= -\cos \gamma_{FQ}, \\ \frac{\partial \gamma_{QF}}{\partial s_F} &= -\frac{\cos \gamma_{FQ}}{QF}, & \frac{\partial \cdot QF}{\partial s_F} &= -\sin \gamma_{FQ}.\end{aligned}\quad (11)$$

Note that  $\gamma_{FQ} \neq \gamma_{QF}$ .

$$\begin{aligned}\frac{\partial}{\partial n_F} (QF \cdot \log QF \cdot \sin \gamma_{QF}) \\ = (1 + \log QF) QF \cdot \sin \gamma_{QF} \frac{\partial \gamma_{QF}}{\partial s_F} - \log QF \cdot \cos \gamma_{QF} \frac{\partial \cdot QF}{\partial s_F}.\end{aligned}\quad (12)$$

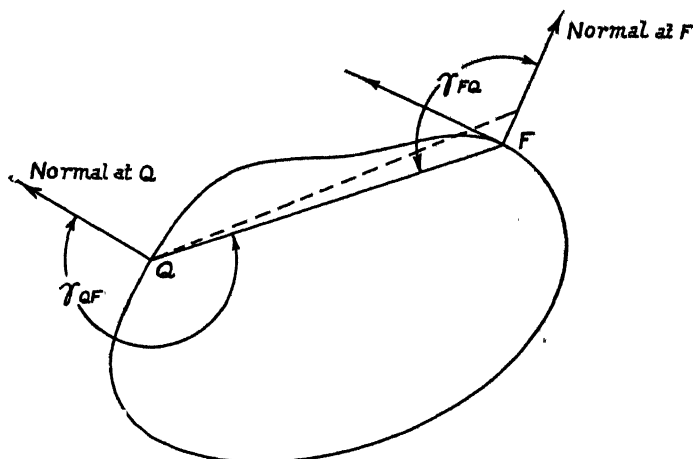


FIG. 2.

Using the values found in (12) to transform (10) gives to the latter the form

$$\begin{aligned}2\pi\psi_M = & \int \left\{ \pi \cdot QM \cdot \log QM \cdot \sin \gamma_{QM} - \frac{1}{2} \int QF \cdot \log QF \cdot \sin \gamma_{QF} d\theta_{FM} \right. \\ & + \frac{1}{2} \int (1 + \log QF) \cdot QF \cdot \sin \gamma_{QF} \cdot \log FM \cdot d\gamma_{QF} \\ & \left. - \frac{1}{2} \int \log QF \cdot \cos \gamma_{QF} \cdot \log FM \cdot d_\tau QF \right\} d\chi_Q \\ & + \int \psi_F d\theta_{FM} - \int \frac{\partial \psi}{\partial n_F} \cdot \log FM \cdot ds_F.\end{aligned}\quad (13)$$

If M be brought on to the boundary (13) becomes a modified integral equation in which  $\chi_Q$  is the only unknown. Once  $\chi_Q$  has been found to satisfy the boundary conditions, equation (13) can be used to find the value of  $\psi_M$  at any point in the region considered.

*The Determination of  $\chi_Q$ .*—It is sufficient to direct attention in the first place to one term only of (13) which may be denoted by

$$\Psi_M = \int QM \cdot \log QM \cdot \sin \gamma_{QM} d\chi, \quad (14)$$

in order to see the method of solution for  $\chi_Q$ . The point M being restricted to lie on the boundary,  $\Psi_M$  may be regarded as a known function of position on that boundary; such position will be defined by a length of perimeter " $s$ " measured from some fixed point. The first operation is to differentiate in (14) with respect to movement of M along the boundary

$$\frac{\partial \Psi}{\partial s_M} = \int \frac{\partial}{\partial s_M} (QM \cdot \log QM \cdot \sin \gamma_{QM}) d\chi_Q. \quad (15)$$

Using expressions similar to those in (11) equation (15) is readily transformed into

$$\frac{\partial \Psi}{\partial s_M} = \int (\log QM \cdot \cos \beta - \sin \gamma_{MQ} \sin \gamma_{QM}) d\chi_Q. \quad (16)$$

As Q passes through M, fig. 3, the angle  $\beta$  passes through zero and  $\cos \beta$  is sensibly equal

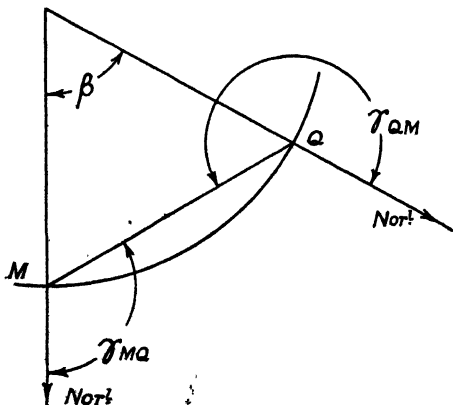


FIG. 3.

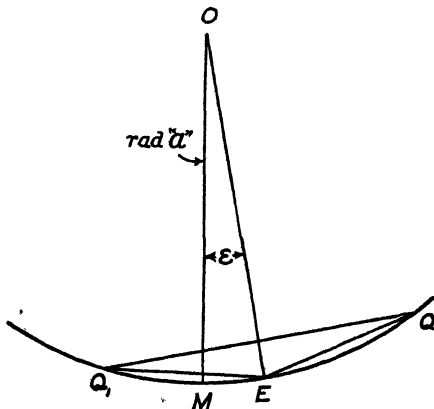


FIG. 4.

to unity for small values of QM. On the other hand,  $\log QM$  is then infinite. The expression  $\sin \gamma_{MQ} \cdot \sin \gamma_{QM}$  is equal to  $-1$  for small values of QM and the existence of this term does not affect the method of solution.

Now assume that

$$\chi_Q = \int \log QE d\Xi_E \quad (17)$$

where  $\Xi_E$  is a function depending on the position of a point E on the boundary. Substituting for  $\chi_Q$  from (17) and changing the order of integration, equation (16) becomes

$$\frac{\partial \Psi}{\partial s_M} = \int \left\{ \int (\log QM \cdot \cos \beta - \sin \gamma_{MQ} \cdot \sin \gamma_{QM}) d\chi_Q \log QE \right\} d\Xi_E. \quad (18)$$

The internal integral of (18) is discontinuous, for as E passes through M there is an abrupt change in the integral from  $-\pi^2/2$  to  $+\pi^2/2$ , no matter what the shape of the boundary. To see this, consider the integral

$$I = \int \log QM \cdot d\chi_Q \log QE \quad (19)$$

in the case where M and E are fixed, fig. 4

In general, for any choice of the point E, two positions Q and Q<sub>1</sub> can be found such that Q<sub>1</sub>E = QE. Taking two elements of (19) together leads to

$$I = \int \log \frac{QM}{Q_1M} d\alpha \log QE, \quad (20)$$

where the limits are from QE = 0 to QE = a maximum value.

As the distance ME is decreased it will be seen that the value of log QM/Q<sub>1</sub>M tends to zero for all pairs of elements at a distance from M large compared with ME. In the limit, when E is indefinitely near M, the sensible elements will all be included in a range of perimeter for which the angle EMQ is small and the points M, E and Q may be taken as lying on the circle of curvature at M.

$$\text{If } Q_1 \text{ lie between M and E} \quad \left. \begin{aligned} QM &= a\epsilon + QE \\ Q_1M &= a\epsilon - QE \end{aligned} \right\} \quad (21)$$

$$\text{If } Q_1 \text{ lie to the left of M} \quad \left. \begin{aligned} QM &= QE + a\epsilon \\ Q_1M &= QE - a\epsilon \end{aligned} \right\} \quad (22)$$

Owing to change of form of expression, the integral I must be considered in two parts

$$QE \text{ from } 0 \text{ to } a\epsilon$$

$$QE \text{ from } a\epsilon \text{ to } a\epsilon \times \infty,$$

and

and the expression becomes

$$I = \int_0^{a\epsilon} \frac{1}{QE} \log \frac{a\epsilon + QE}{a\epsilon - QE} d\alpha \cdot QE + \int_{a\epsilon}^{a\epsilon \times \infty} \frac{1}{QE} \log \frac{QE + a\epsilon}{QE - a\epsilon} d\alpha \cdot QE. \quad (23)$$

Write  $x$  for  $QE/a\epsilon$  in the first integral and  $1/x$  for  $QE/a\epsilon$  in the second. The two integrals are found to have the same value and are independent of the radius of curvature " $a$ ." Equation (23) becomes

$$I = 2 \int_0^1 \frac{1}{x} \log \frac{1+x}{1-x} dx, \quad (24)$$

I is a definite integral of the Gamma function series and its value is  $\pi^2/2$ . Had E been on the other side of M the sign of I would have been changed.

Owing to the discontinuity in I as shown above, the form of (18) can be changed by a partial integration with respect to variation of E; the result lends itself to an expansion for  $\Xi$ . The form is

$$\frac{\partial \Psi}{\partial \Xi_M} = \pi^2 \Xi_M + \int_{\pi^2/2}^{-\pi^2/2} \Xi d\alpha \left\{ \int (\log QM \cos \beta - \sin \gamma_{QM} \cdot \sin \gamma_{QM}) d\alpha \log QE \right\}, \quad (25)$$

and  $\Xi_M$  is found by successive substitution.

In order to shorten the notation when returning to equation (13) we write

$$\omega_M \text{ for } 2\pi\psi_M - \int \psi_F d\theta_{FM} + \int \frac{\partial \psi}{\partial n_F} \log FM \cdot d\theta_F \quad (26)$$

and

$$\begin{aligned} Y_{MQ} \text{ for } & \pi \cdot QM \cdot \log QM \cdot \sin \gamma_{QM} - \frac{1}{2} \int QF \cdot \log QF \cdot \sin \gamma_{QF} \cdot d\theta_F \theta_{FM} \\ & + \frac{1}{2} \int (1 + \log QF) QF \cdot \sin \gamma_{QF} \cdot \log FM \cdot d\theta_F \gamma_{QF} \\ & - \frac{1}{2} \int \log QF \cdot \cos \gamma_{QF} \cdot \log FM \cdot d\theta_F \cdot QF, \end{aligned} \quad (27)$$

so that equation (13) becomes

$$\varpi_M = \int Y_{MQ} d\chi_Q, \quad (28)$$

and combining this with (17)

$$\varpi_M = \int \{ \int Y_{MQ} \cdot d_Q \log QE \} d\Xi_E, \quad (29)$$

$$\frac{\partial \varpi}{\partial s_M} = \int \left\{ \int \frac{\partial Y_{MQ}}{\partial s_M} \cdot d_Q \log QE \right\} d\Xi_E, \quad (30)$$

and by the use of a theorem similar to (25)

$$\frac{\partial \varpi}{\partial s_M} = -\frac{\pi^3}{2} \Xi_M + \int_{\pi^3/4}^{-\pi^3/4} \Xi_E d_E \left\{ \int \frac{\partial Y_{MQ}}{\partial s_M} d_Q \cdot \log QE \right\}. \quad (31)$$

Rearranging the terms

$$\frac{\pi^3}{2} \Xi_M = -\frac{\partial \varpi}{\partial s_M} + \int_{\pi^3/4}^{-\pi^3/4} \Xi_E d_E \left\{ \int \frac{\partial Y_{MQ}}{\partial s_M} d_Q \log QE \right\}, \quad (32)$$

and by successive substitution  $\Xi_M$  may be found.

The series for  $\Xi_M$  must of course be convergent if it is to be useful; but no proof of convergency has been attempted.

This completes the general account of the analysis.

*Scope of the Application of the preceding Solution of the Equation  $\nabla^4 \psi = 0$ .*

The physical problems which can be solved by the method outlined up to the present point appear to be those of the flexure of a thin flat plate internal to a given boundary. This boundary may be of any shape in three dimensions except for the limitation that the co-ordinate normal to the mean plane of the boundary must be small. The slope of the plate at the boundary is also arbitrary within the same limits. By means of the theorems relating to particular integrals, the solution of the flexural problems may be extended to the further stage of an arbitrary loading over the enclosed area.

If an attempt be made to apply the analysis to the part of infinite space external to the boundary, difficulties are encountered and the analogous problems in the slow motion of a body through a viscous fluid are included in this class. It has already been pointed out by Sir G. G. Stokes and Prof. Lamb\* that no solution appears to be possible for the steady motion of a cylinder through an infinite expanse of fluid stationary at infinity. It is not difficult so to modify (8) that the condition  $\psi = 0$  is satisfied at infinity and to examine the equation for the value of  $\chi$ . Failure—in the case of a circular cylinder—occurs by numerical equality, but with incompatible signs in one or other of the quantities  $\psi$  or  $\partial\psi/\partial n$  on the boundary.

It appeared from considerations of the above difficulties that progress with

\* Lamb, 'Hydrodynamics,' pp. 603 and 604.

the fluid motion problems would require an extension of the analysis to double boundaries, and the method previously found effective for the solution of  $\nabla^2\psi = 0$  in an earlier paper\* was again tried and has led to the solution given below. The increased labour involved in dealing with double boundaries instead of single ones is considerable.

*Slow Motion of a Viscous Fluid through a Parallel-walled Channel and past a Circular Cylinder.*

It has not been found to be necessary to restrict the outer boundary to finite distances from the cylinder at all points, and in the direction of flow infinite length is retained.

The details of the slow motion in a parallel channel are well known and may be found in standard treatises,† and the molecular rotation found to be proportional to the distance from the centre line of the channel. Since (6) is only valid for a molecular rotation which vanishes at infinity, this uniform streaming has been eliminated from the problem as an initial step and the difference due to the cylinder separately estimated. As solutions of the equation  $\nabla^4\psi = 0$  are additive, the two problems are very simply related.

The procedure, then, is:—

(1) Ignoring the parallel walls of the channel, find a solution of  $\nabla^4\psi = 0$  which satisfies the required boundary conditions at the surface of the cylinder. In the case of the circular cylinder this is readily obtained by expressing  $\zeta$  in spherical harmonics, but in any other case the method indicated in equations (26)–(32) is available. In general it appears that  $\psi$  will tend to become infinite at an infinite distance from the cylinder.

(2) Find the values of  $\psi$  and  $\partial\psi/\partial n$  from this solution at the position of the outer boundary and ignoring the inner boundary, apply equations (26)–(32) to find a solution of  $\nabla^4\psi = 0$  which has equal and opposite values for  $\psi$  and  $\partial\psi/\partial n$  at the outer boundary.

(3) Combine the solutions of (1) and (2) by addition so as to give  $\psi$  and  $\partial\psi/\partial n$  on the outer boundary. In general the conditions on the cylinder will not then be satisfied (in our example a very close approximation is obtained at this stage), and the difference between the required and calculated values forms a new starting point for a repetition of the process.

The process lacks the precision of equations (26)–(32), but appears to be quite satisfactory in application; our present example supports the earlier one based on  $\nabla^2\psi = 0$  in indicating convergency. Connection between the two is not wholly lacking since the molecular rotation satisfies the equation

\* ‘Roy. Soc. Proc.’ A, vol. 95, p. 464 (1919).

† Lamb, ‘Hydrodynamics,’ p. 576.

$\nabla^2 \zeta = 0$ , and it is the strength of the  $\zeta$  doublets which is found by the present analysis.

The remainder of this paper is devoted to a detailed consideration of the solution of a particular problem.

*Initial Conditions.*

A cylinder of unit radius is fixed relative to the parallel walls of a channel so that its centre is five units away from each wall. Fluid is forced through the channel in quantity sufficient to give unit velocity to the fluid in the centre of the channel at infinity. Absence of relative motion between the fluid and solid boundaries is taken as a condition of viscous fluid motion. Incompressibility of the fluid is assumed.

The differential equation of motion to be satisfied is

$$\nabla^4 \psi_1 = 0. \quad (33)$$

Along the cylinder

$$\psi_1 = 0 \quad \text{and} \quad \frac{\partial \psi_1}{\partial n} = 0. \quad (34)$$

Whilst along the outer boundaries

$$\psi_1 = \pm \alpha \quad \text{and} \quad \frac{\partial \psi_1}{\partial n} = 0, \quad (35)$$

where  $\alpha$  is determined from the width of the channel and the hypothesis that at infinity, where the flow is laminar, the velocity at the centre is unity.

Corresponding with the special conditions of the problem, we have at infinity

$$\psi_2 = -y \left\{ 1 - \frac{1}{8} \left( \frac{y}{b} \right)^2 \right\}, \quad (36)$$

where  $2b$  is the distance between the two walls, *i.e.*, is equal to 10 (see fig. 5). Writing  $\psi + \psi_2$  for  $\psi_1$ , equation (33) is replaced by

$$\nabla^4 \psi = 0, \quad (37)$$

$\psi = 0$  and  $\partial \psi / \partial n = 0$  on each of the walls of the channel.

On the cylinder it is easily found that

$$\left. \begin{aligned} \psi &= \sin \theta \left( 1 - \frac{\sin^2 \theta}{3b^2} \right) \\ \frac{\partial \psi}{\partial n} &= \sin \theta \left( 1 - \frac{\sin^2 \theta}{b^2} \right) \end{aligned} \right\}. \quad (38)$$

For the cylinder the normal into the fluid has been chosen in fixing the sign of  $n$ .  $\theta$  is measured from the centre of the cylinder and a line midway between the walls.

Ignoring the conditions at the outer boundary, a solution of (37) compatible with (38) is obtained by expressing  $\zeta$  in terms of spherical harmonics; it being assumed that

$$\psi = Ar \sin \theta \cdot \log r + \frac{B \sin 3\theta}{r} + \frac{E \sin \theta}{r} + \frac{D \sin 3\theta}{r^3}. \quad (39)$$

From (38) the values of A, B, C and D are found and give to  $\psi$  the value

$$\psi = \left(2 - \frac{1}{b^2}\right) r \sin \theta \cdot \log r + \left(1 - \frac{1}{4b^2}\right) \frac{\sin \theta}{r} + \frac{\sin 3\theta}{4b^2 r} \left(1 - \frac{2}{3r^2}\right), \quad (40)$$

over the whole field. The values of  $\psi$  and  $\partial\psi/\partial n$  are required for the position of the outer boundary.

The convenient co-ordinates being K and  $b$ , the value of  $\psi$  on the outer boundary is

$$\psi = \left(b - \frac{1}{2b}\right) \log (K^2 + b^2) + \left(b + \frac{1}{2b}\right) \left\{ \frac{1}{K^2 + b^2} - \frac{1}{(K^2 + b^2)^2} \right\} + \frac{b}{3(K^2 + b^2)^3}. \quad (41)$$

In developing the formula (13) the outward normal was used and hence

$$\frac{\partial\psi}{\partial n} = \frac{\partial\psi}{\partial b} \quad (42)$$

for the outer boundary. Hence  $\partial\psi/\partial n$  is found from (41) without difficulty.

The next step is to obtain a solution of the equation (13) as applied to the parallel walls. Using  $\varpi_M$  and  $Y_{Mq}$  as defined in equations (26) and (27) the solution of

$$\varpi_M = \int Y_{Mq} d\chi_q \quad (43)$$

is required when M is on the boundary wall. It is convenient for later use to determine the value of  $\varpi_M/\pi - 2\psi_M$  in a form suitable for points in the fluid, and two new variables,  $b_1$  and  $b_2$ , are introduced and defined in fig. 5.

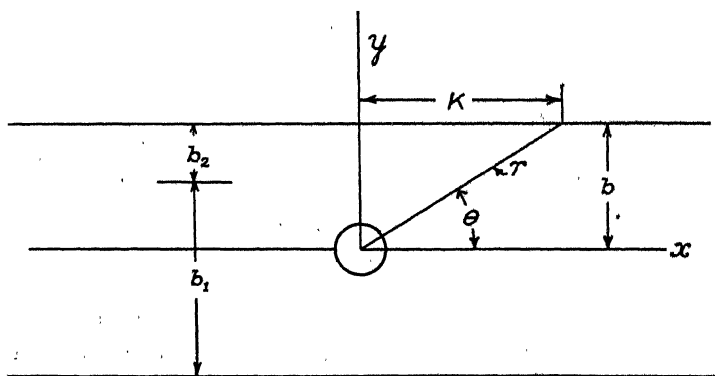


FIG. 5.

The value of

$$\frac{\varpi_M}{\pi} - 2\psi_M \equiv -\frac{1}{\pi} \int \psi_P d\theta_{PM} + \frac{1}{\pi} \int \frac{\partial \psi}{\partial n_P} \log PM ds_P \quad (44)$$

is found by taking the two line integrals together, and in general terms leads to

$$\begin{aligned} \frac{\varpi_M}{\pi} - 2\psi_M = & \left(1 - \frac{1}{2b^2}\right) \left\{ (b_2 + b) \log (K^2 + \overline{b_2 + b})^2 - (b_1 + b) \log (K^2 + \overline{b_1 + b})^2 \right. \\ & \left. - 2(b_1 - b_2) - 2K \left( \tan^{-1} \frac{K}{b_2 + b} - \tan^{-1} \frac{K}{b_1 + b} \right) \right\} \\ & + \frac{b_2 + b}{2b^2(K^2 + \overline{b_2 + b})^2} - \frac{b_1 + b}{2b^2(K^2 + \overline{b_1 + b})^2} \end{aligned} \quad (45)$$

as a close approximation. In calculating numerical values from (41) it appeared that certain terms were very small and in order to reduce the length of the expressions they have been omitted in this example.

When M is on the top right boundary—symmetry makes it unnecessary to consider the whole boundary in detail—the value of  $\psi_M$  is to be equal to that given by (41). Putting  $b_1 = 10$ ,  $b_2 = 0$  and  $b = 5$  in (45) a value of  $\varpi/\pi$  is obtained which by differentiation with respect to K gives  $1/\pi \partial \varpi / \partial s$  required in the solution for  $\Xi$  by the methods outlined in the earlier part of the paper. The analytical expressions are

$$\begin{aligned} \frac{\varpi}{\pi} = & 0.98 \left\{ 15 \log \frac{K^2 + 25}{K^2 + 225} + 20 - 2K \left( \tan^{-1} \frac{K}{5} - \tan^{-1} \frac{K}{15} \right) \right\} \\ & + \frac{10.3}{K^2 + 25} - \frac{10.2}{(K^2 + 25)^2} + \frac{20}{(K^2 + 25)^3} - \frac{0.3}{K^2 + 225} \end{aligned} \quad (46)$$

and

$$\begin{aligned} \frac{1}{\pi} \frac{\partial \varpi}{\partial s_M} = & 0.98 \left\{ 2 \left( \tan^{-1} \frac{K}{5} - \tan^{-1} \frac{K}{15} \right) - \frac{20K}{K^2 + 25} \right\} \\ & - \frac{20.6K}{(K^2 + 25)^2} - \frac{40.8K}{(K^2 + 25)^3} + \frac{40K}{(K^2 + 25)^4} - \frac{0.6K}{(K^2 + 225)^2} \end{aligned} \quad (47)$$

Without evaluating  $\Xi_M$  an approximation to  $\chi_Q$  can be obtained by making use of the fact that when  $\chi_Q$  is linear between two fixed abscissæ for Q this segment of  $\chi_Q$  contributes to the integral  $\int Y_{MQ} dQ$  for a fixed point, M, a quantity proportional to the slope of the segment. This enables a polygonal form for  $\chi_Q$  to be determined such that the integrals for any chosen points, M, shall have any required values. In the special case considered the abscissæ of the angular points of the polygon were taken at  $k = 0, 5, 10, 15$  and the chosen positions of M at  $K = 0, 5, 10, 20$ . Owing to the symmetrical form of  $\chi_Q$  the slope of a side in one quadrant determined a side in each of the other three quadrants. The contributions to the integral due to each



group of four sides were calculated for the chosen positions of  $M$  on the hypothesis that the sides in one quadrant had unit slope. Four simultaneous equations then determined the multiples of these contributions—and therefore the slopes of the sides—necessary to give  $\varpi_M$  the required values at the four positions of  $M$  selected. In the special case considered the contributions for unit slope were calculated analytically, but in general they would have to be ascertained graphically. In each quadrant the polygonal form determined as above approximated to a straight line. In order to avoid discontinuity the straight line was replaced by an arc of a parabola from  $k = 0$  to  $k = 2.5$ , and then by the tangent to this parabola. For positions of  $M$  other than those selected the values of  $\varpi_M$  corresponding to the  $\chi_Q$  thus determined were fairly good approximations to those required, but in order to get a closer agreement a small additional term of the type  $2a/a^2 + k^2$  was introduced and the constants were suitably adjusted; the form of the modifications from the straight line was determined by considerations of symmetry and ease of analytical manipulation.

A value of  $\chi_Q$  which satisfies (43) very closely is given by

$$\chi_Q = \frac{26.15}{k^2 + 25} - 0.05937k^2, \quad k \text{ between } 0 \text{ and } 2.5$$

$$\text{and} \quad \chi_Q = \frac{26.15}{k^2 + 25} - 0.05937(5k - 6.25), \quad k \text{ between } 2.5 \text{ and } 0. \quad (48)$$

The degree of closeness of the approximation can be seen from Table I which shows the value of  $-\varpi/\pi$  as calculated from (48) and (45) in comparison with the value required. The form chosen is integrable generally for  $\varpi/\pi$  in the fluid. The approximation could be further elaborated if required.

The finding of  $\chi_Q$  as given by (48) is the essential part of the solution of the second stage of the problem of the flow of fluid past a circular cylinder in a parallel-walled channel. Corresponding with (48) is a somewhat lengthy expression:—

$$\begin{aligned} -\frac{\varpi_M}{\pi} = & 2.615 \left[ \log \frac{K^2 + \overline{b_1 + 5}^2}{K^2 + \overline{b_2 + 5}^2} \cdot \frac{K^2 + \overline{b_1 + 15}^2}{K^2 + \overline{b_2 + 15}^2} - \frac{4b_1(b_1 + 5)}{K^2 + \overline{b_1 + 5}^2} + \frac{4b_2(b_2 + 5)}{K^2 + \overline{b_2 + 5}^2} \right] \\ & + \frac{0.05937}{6} \left[ \frac{2.5 + K}{2} \left\{ (\overline{2.5 + K}^2 + 9b_2^2) \log (\overline{2.5 + K}^2 + b_2^2) \right. \right. \\ & \quad \left. \left. - (\overline{2.5 + K}^2 + 9b_1^2) \log (\overline{2.5 + K}^2 + b_1^2) \right. \right. \\ & \quad \left. + (\overline{2.5 + K}^2 - 3 \cdot \overline{b_2 + 10}^2) \log (\overline{2.5 + K}^2 + \overline{b_2 + 10}^2) \right. \\ & \quad \left. \left. - (\overline{2.5 + K}^2 - 3 \cdot \overline{b_1 + 10}^2) \log (\overline{2.5 + K}^2 + \overline{b_1 + 10}^2) \right\} \right] \end{aligned}$$

$$\begin{aligned}
 & + \frac{2.5-K}{2} \left\{ (\overline{2.5-K}^2 + 9b_2^2) \log (\overline{2.5-K}^2 + b_2^2) \right. \\
 & \quad - (\overline{2.5-K}^2 + 9b_1^2) \log (\overline{2.5-K}^2 - b_1^2) \\
 & + (\overline{2.5-K}^2 - 3 \cdot \overline{b_2+10}^2) \log (\overline{2.5-K}^2 + \overline{b_2+10}^2) \\
 & \quad \left. - (\overline{2.5-K}^2 - 3 \cdot \overline{b_1+10}^2) \log (\overline{2.5-K}^2 + \overline{b_1+10}^2) \right\} \\
 & + b_2 (5b_2^2 - 3 \cdot \overline{2.5+K}^2) \tan^{-1} \frac{2.5+K}{b_2} \\
 & \quad - b_1 (5b_1^2 - 3 \cdot \overline{2.5+K}^2) \tan^{-1} \frac{2.5+K}{b_1} \\
 & - (b_2+10) (\overline{b_2+10}^2 - 3 \cdot \overline{2.5+K}^2) \tan^{-1} \frac{2.5+K}{b_2+10} \\
 & \quad + (b_1+10) (\overline{b_1+10}^2 - 3 \cdot \overline{2.5+K}^2) \tan^{-1} \frac{2.5+K}{b_1+10} \\
 & + b_2 (5b_2^2 - 3 \cdot \overline{2.5-K}^2) \tan^{-1} \frac{2.5-K}{b_2} \\
 & \quad - b_1 (5b_1^2 - 3 \cdot \overline{2.5-K}^2) \tan^{-1} \frac{2.5-K}{b_1} \\
 & - (b_2+10) (\overline{b_2+10}^2 - 3 \cdot \overline{2.5-K}^2) \tan^{-1} \frac{2.5-K}{b_2+10} \\
 & \quad + (b_1+10) (\overline{b_1+10}^2 - 3 \cdot \overline{2.5-K}^2) \tan^{-1} \frac{2.5-K}{b_1+10} \\
 & - 200 (b_1 - b_2) \Big]. \tag{49}
 \end{aligned}$$

Table I.—Outer Boundary.

K.	From (44) — $w_M/\pi$ .	From (48) — $w_M/\pi$ .	From (41) $\partial\psi/\partial n_M$ .	From (45) and (48) $\partial\psi/\partial n_M$ .
0	12.30	12.30	5.06	5.07
5	8.39	8.39	—	4.80
10	4.49	4.53	5.12	5.12
15	2.62	2.65	—	5.60
20	1.75	1.68	6.05	6.04
30	0.83	0.82	6.73	6.73
40	—	—	7.27	—
50	0.33	0.33	7.70	—

The next step is the calculation of  $\psi_M$  and  $\partial\psi/\partial n_M$  from (45) and (48) when the point M lies on the inner circular boundary. Points being defined as before by the angle  $\theta$ , measured at the centre of the circle, the result of the calculation is given in Table II. Since it is of interest to examine the effect of molecular rotation, the elements of  $\psi_M$  and  $\partial\psi/\partial n_M$  which depend

on  $\chi$  and those which are independent of it are separately tabulated as well as the sum.

Table II.—Inner Boundary (due to Sources on Outer Boundary).

$\theta^\circ$ .	From (48) $-\psi_M/\pi$ .	From (45) $2\psi - \psi_M/\pi$ .	$\psi_M$ .	From (48) $-1/\pi \partial\psi/\partial n_M$ .	From (45) $\partial/\partial n_M (2\psi - \psi/\pi)$ .	$\partial\psi/\partial n_M$ .
0	0	0	0	0	0	0
10	0.73	1.57	0.42	0.693	1.576	0.441
20	1.40	3.09	0.85	1.358	3.104	0.873
30	2.05	4.52	1.25	1.994	4.500	1.253
40	2.67	5.81	1.57	2.570	5.790	1.610
50	3.17	6.92	1.79	3.048	6.882	1.892
60	3.59	7.82	2.11	3.460	7.780	2.160
70	3.90	8.48	2.29	3.784	8.489	2.352
80	4.09	8.88	2.40	3.982	8.880	2.424
90	4.16	9.02	2.43	4.035	9.007	2.486

Within the limits of accuracy of working, the above figures are represented by

$$\left. \begin{aligned} \psi_M &= 2.44 \sin \theta + 0.01 \sin 3\theta \\ \text{and} \quad \frac{\partial \psi}{\partial n_M} &= 2.48 \sin \theta + 0.02 \sin 3\theta \end{aligned} \right\}, \quad (50)$$

i.e., the values are very nearly proportional to  $\sin \theta$ , with the constants of proportionality almost the same.

Very little further work completes the calculation to the full degree of accuracy hitherto attempted. Two values of  $\psi$  have been found which satisfy the differential equation  $\nabla^2 \psi = 0$ , but with different, though related, boundary conditions. As in (38) and (40), define one of these by  $\psi$ , and as in (44) and (45), define the second by  $\psi_M$ . The first represents the solution which satisfies the inner boundary conditions and ignores the outer boundary, whilst the second has the same values as the first at the outer boundary, but has not involved direct consideration of the inner boundary.

On the channel walls therefore

$$\frac{\partial \psi}{\partial n_M} = \frac{\partial \psi}{\partial n}, \quad \psi_M = \psi. \quad (51)$$

On the inner boundary, close approximations are

$$\left. \begin{aligned} \psi &= 0.990 \sin \theta + 0.003 \sin 3\theta \\ \psi_M &= 2.440 \sin \theta + 0.010 \sin 3\theta \end{aligned} \right\}, \quad (52)$$

$$\left. \begin{aligned} \frac{\partial \psi}{\partial n} &= 0.970 \sin \theta + 0.010 \sin 3\theta \\ \frac{\partial \psi}{\partial n_M} &= 2.480 \sin \theta + 0.020 \sin 3\theta \end{aligned} \right\}. \quad (53)$$

The function  $\gamma(\psi_M - \psi)$  can, by choice of  $\gamma$ , be made to satisfy the boundary conditions on the cylinder approximately, whilst those on the channel walls are completely satisfied. It is, however, easy to carry the accuracy further by the use of spherical harmonic functions which vanish at infinity and are of the order of accuracy of working on the outer boundary. It is assumed, therefore, that

$$\psi_3 = \gamma(\psi_M - \psi) + \alpha \frac{\sin \theta}{r} + \beta \frac{\sin 3\theta}{r^3} \quad (54)$$

is to be made to approximate to the boundary values as closely as possible by choice of  $\gamma$ ,  $\alpha$ , and  $\beta$ . The algebraic work is simple and

$$\psi_3 = 0.662(\psi_M - \psi) + 0.030 \frac{\sin \theta}{r} - 0.001 \frac{\sin 3\theta}{r^3}, \quad (55)$$

gives boundary values on the cylinder of

$$\left. \begin{aligned} \psi_3 &= 0.990 \sin \theta + 0.004 \sin 3\theta \\ \frac{\partial \psi_3}{\partial n} &= 0.970 \sin \theta + 0.010 \sin 3\theta \end{aligned} \right\}, \quad (56)$$

and, by comparison with those postulated for  $\psi$  (see (52) and (53)), the accuracy is seen to be complete to the order attempted in the previous Tables. On the outer boundary the effect of the added spherical harmonic terms is small and does not exceed 0.006 in the value of  $\psi_3$  at any point.

To complete the solution, it is necessary to add that corresponding with steady streaming of the fluid through the unobstructed channel, as given by (36), *i.e.*, the final stream function is

$$\begin{aligned} 0.662 \left\{ \psi_M - 1.96r \sin \theta \log r - 0.990 \frac{\sin \theta}{r} - \frac{\sin 3\theta}{100r} \left( 1 - \frac{2}{3r^2} \right) \right\} \\ + 0.030 \frac{\sin \theta}{r} - 0.001 \frac{\sin 3\theta}{r^3} - r \sin \theta \left( 1 - \frac{r^2 \sin^2 \theta}{75} \right), \quad (57) \end{aligned}$$

and  $\psi_M$  is defined by equations (45) and (48).

From (57) were calculated values of the stream function, from which fig. 6 was prepared.

The value of the stream function given by (57) applies to the case of the flow of fluid through a channel past a circular cylinder. There is a slightly different flow when the cylinder is moved at uniform velocity through stationary fluid, and it is perhaps worth while to deduce an approximate expression for  $\psi$  in the latter case. Strictly calculated, the new problem calls for a solution of the differential equation (37) with boundary values

$$\left. \begin{aligned} \psi &= \sin \theta \\ \frac{\partial \psi}{\partial n} &= \sin \theta \end{aligned} \right\} \quad (38a)$$

instead of (38). It is, however, evident that the differences between the two sets of conditions are very small, being less than 2 per cent. for  $\psi$  and 4 per

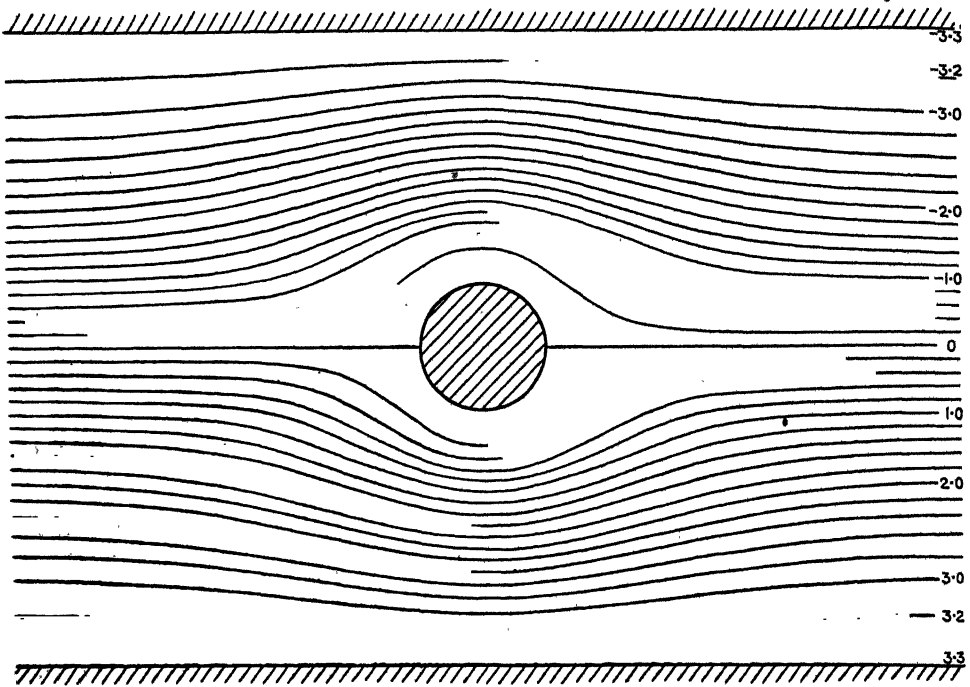


FIG. 6.—Stream lines ( $\psi$ ).

cent. for  $\partial\psi/\partial n$ . It might then be expected that many of the succeeding expressions would differ by similar small amounts. This is seen to be true for the equivalent of equation (40), which is

$$\psi = 2r \sin \theta \log r + \frac{\sin \theta}{r}. \quad (40a)$$

On the cylinder walls  $r$  is unity, whilst the least value on the channel walls is 5. The same reasoning leads to the hypothesis that  $\psi_M$  is sensibly the same as that given by (50), and in producing equation (58) the small terms in  $\sin 3\theta$  in equation (50) were ignored. Following the method indicated in equations (54) to (57) a new value for the stream function is obtained as

$$\psi_4 = 0.676 \left\{ \psi_M - 1.96r \sin \theta \log r - 0.990 \frac{\sin \theta}{r} \right\} + \frac{0.020 \sin \theta}{r} \quad (58)$$

and the value of all the numerical approximations may be tested *a posteriori*. On the cylinder the values of  $\psi_M$  and  $\partial\psi/\partial n_M$  are given by (50), and putting  $r = 1$  in (58) leads to

$$\psi_4 = \sin \theta + 0.007 \sin 3\theta \quad (59)$$

which is very close to the required value. Similar calculations show that the remaining boundary conditions, both on the cylinder and channel walls, are equally closely approached.

Since the relative motion of the fluid and cylinder when the latter moves is very little different from that when the fluid moves, it follows that the calculated resistance will be given approximately by the same expression (68).

*Calculation of  $\zeta$  and the Resistance of the Cylinder.*

The value of  $\zeta$  may be obtained from (57) by differentiation, but it is simpler in the present instance to determine  $\zeta_m$  directly from the value of  $\chi$ . Before integration the expression for  $\zeta_m$  is

$$\zeta_m = 0.662 \left\{ \int \frac{\sin \gamma_{QM}}{QM} d\chi_Q - 3.92 \frac{\sin \theta}{r} - 0.08 \frac{\sin 3\theta}{r^3} \right\} + 0.08r \sin \theta. \quad (59a)$$

The value of  $\int \frac{\sin \gamma_{QM}}{QM} d\chi_Q$  was found analytically and the necessary calculations were made for the drawing of fig. 7.

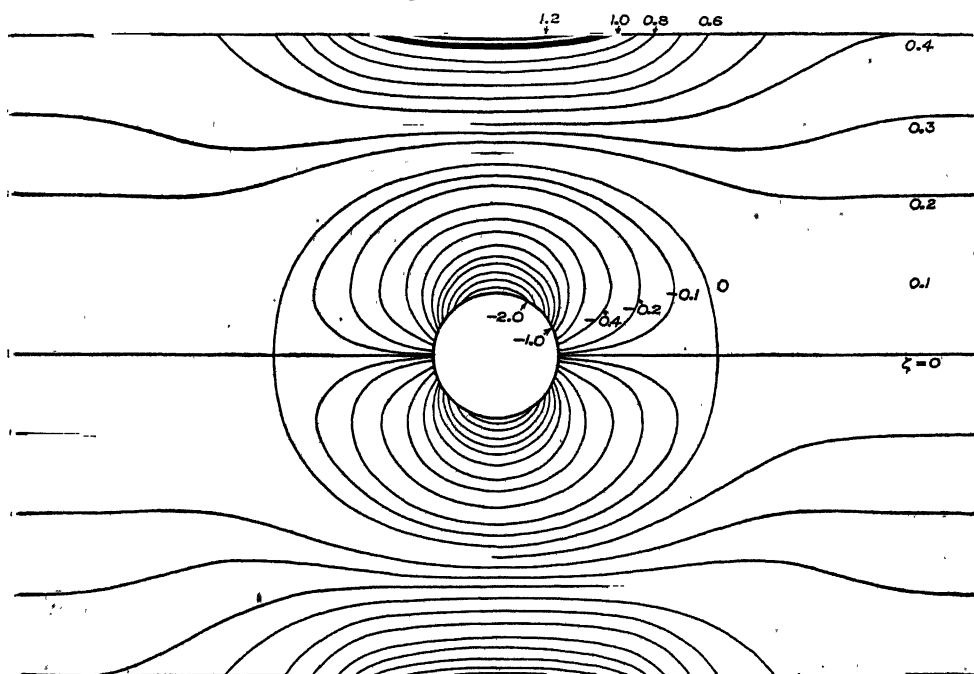


FIG. 7.—Lines of constant molecular rotation ( $\zeta$ ).

On the inner boundary it was found that a close approximation to  $\zeta$  is given by

$$\zeta_{\text{cylinder}} = -2.32 \sin \theta - 0.053 \sin 3\theta \quad (60)$$

and this value was used in estimating the resistance of the cylinder.

The formulæ for the pressures were taken from Lamb's 'Hydrodynamics,' p. 570, and with the fluid incompressible are

$$\left. \begin{aligned} p_{xx} &= -p + 2\mu \frac{\partial u}{\partial x} \\ p_{yy} &= -p + 2\mu \frac{\partial v}{\partial y} \\ p_{yz} &= p_{xy} = \mu \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \end{aligned} \right\} \quad (61)$$

where  $p$  is to be obtained from the relations

$$\frac{\partial p}{\partial x} = -\mu \frac{\partial \zeta}{\partial y}, \quad \frac{\partial p}{\partial y} = +\mu \frac{\partial \zeta}{\partial x}. \quad (62)$$

It is not difficult to show that

$$\frac{p}{\mu} = 0.662 \left\{ \int \frac{\cos \gamma_{QM}}{QM} d\chi_Q - 3.92 \frac{\cos \theta}{r} - 0.08 \frac{\cos 3\theta}{r^3} \right\} + 0.08r \cos \theta, \quad (63)$$

and the evaluation on the inner boundary admits of the expression

$$p = \mu (2.32 \cos \theta + 0.053 \cos 3\theta) \quad (64)$$

being used as of sufficient accuracy.

Since  $\zeta = \partial^2 \psi / \partial r^2$  on the cylinder and the velocities along and normal to the surface are zero, it is easy to find the differential coefficients  $\partial u / \partial x$ , etc., and hence  $p_{xx}$  and  $p_{xy}$ .

The resistance of the cylinder per unit length is then

$$R = - \int_0^{2\pi} p_{xx} \cos \theta d\theta + \int_0^{2\pi} p_{xy} \sin \theta d\theta. \quad (65)$$

It appears that the integrals contribute equal amounts to the resistance, which is, in numerical form

$$R = 2.26 \pi \mu. \quad (66)$$

It should here be noted that the cylinder is of unit radius and that the free-stream velocity in the middle of the channel is unity. The formula for resistance is easily generalised, for on the principles of dynamical similarity

$$\frac{Rd}{\rho U^2 d^2} = f \left( \frac{Ud}{\nu} \right) \quad (67)$$

where  $U$  is the stream velocity,  $d$  the diameter of the cylinder and  $\nu$  the kinematic viscosity ( $\rho\nu = \mu$ ) and  $\rho$  the density of the fluid. Since  $R$  is proportional to  $\mu$  it follows that  $f(Ud/\nu)$  must take the form  $A\nu/Ud$  where  $A$  is a constant to be determined from (66). It is then found that

$$\frac{Rd}{\rho U^2 d^2} = 7.10 \frac{\nu}{Ud} \quad (68)$$

The limitations imposed on the application of the formula are discussed by Lamb and it appears that  $Ud/\nu$  should not greatly exceed 0.2 if (68) is to apply. The resistance coefficient  $Rd/\rho U^2 d^2$  is 35.5 when  $Ud/\nu = 0.2$ .

Observations in a wind channel have not been made at values less than  $Ud/\nu = 10$ , and the corresponding resistance coefficient is then 1.5, but is varying rapidly in the direction leading to high values at low values of  $Ud/\nu$ . It may be noted as of interest that the formula given above (68) would give a coefficient of 0.71 at  $Ud/\nu = 10$ , *i.e.*, about half the observed value. The departure from fact is then less than might have been anticipated on mathematical grounds.

The resistance of a cylinder in a viscous fluid of infinite extent has been worked out by Oseen,\* using a different equation of motion, but subject to the same physical and mathematical limitations as in the present problem. The resistance as given by Lamb is

$$\frac{Rd}{\rho U^2 d^2} = \frac{4\pi \cdot \nu / Ud}{1.309 - \log Ud/\nu}, \quad (69)$$

and when  $Ud/\nu = 0.2$  the value of  $Rd/\rho U^2 d^2$  is 21.6. It is not possible to use the formula for higher values of  $Ud/\nu$  on account of the analytical form, since the assumption that  $Ud/\nu$  is small has been used both in forming the equations of motion and also in solving them. It appears to be probable that the latter limitation can be removed by methods similar to those of the present paper. For the moment it may be noted that the presence of a channel only five times the diameter of the cylinder in width has not raised the resistance to double that in a free stream.

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\* Lamb, 'Hydrodynamics,' pp. 605-607.



*The Law of Distribution of Particles in Colloidal Solution.*

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*I. Introduction.*

The work of Perrin and his collaborators (1) on the experimental and theoretical application of the results of the kinetic theory to colloidal solutions is probably the most complete exposition of this very interesting phase of modern work. In the course of the work, Perrin (2) shows that we should expect a law of distribution of the particles in a colloidal suspension analogous to that regulating the distribution of the molecules of air in the atmosphere.

By balancing the osmotic pressure of the particles in solution against the effect of gravity, he deduces the equation

$$\frac{RT}{N} \log \frac{n}{n_0} = V(\rho_1 - \rho_2)g(h - h_0), \quad (1)$$

where  $n$  and  $n_0$  are the numbers of particles per cubic centimetre, at depths  $h$  and  $h_0$  from the top of the solution,

$V$  is the volume of each particle,

$\rho_1$  and  $\rho_2$ , the densities of the material of the particles and the medium respectively,

and  $R$ ,  $T$ ,  $N$ , and  $g$  the ordinary constants.

Perrin tests the reliability of this equation by observations from which he quotes two typical series:—

1. For gamboge particles  $2.12 \times 10^{-5}$  cm. in diameter, the number of particles at four different depths differing successively by  $3 \times 10^{-3}$  ( $30 \mu$ ) were found to be proportional to the numbers

$$12 : 22.6 : 47 : 100$$

which numbers are almost the same as the geometrical progression

$$11.1 : 23 : 48 : 100.$$

2. For gamboge particles  $5.2 \times 10^{-5}$  cm. in diameter, similar observations of depths differing by  $6 \times 10^{-4}$  cm. ( $6 \mu$ ) gave numbers proportional to

$$305 : 530 : 940 : 1880$$

approximately given by

$$280 : 528 : 995 : 1880$$

which are in geometrical progression.

If the above equation be written

$$\log \frac{n}{n_0} = P(h-h_0) \text{ where } P = \frac{N}{RT} \cdot V \cdot (\rho_1 - \rho_2) \cdot g, \quad (2)$$

the two series of results give values for P as follows:

$$\text{I } P_1 = 100, \quad \text{II } P_2 = 500.$$

As pointed out by Perrin, the concentration at a distance  $9.6 \times 10^{-3}$  cm. from the bottom of the dish would only be 1/60,000 of that at the bottom, and he adds, "hence, when permanent equilibrium has been reached, grains will hardly ever be found in the higher layers of such preparations."

Using the value of P as obtained above, we can easily find by calculation that the increase in concentration down a tube of a few centimetres depth would be an enormous multiple of the concentration at the top.

Perrin's experiments were carried out on gamboge particles, which were very large compared with the particles of ordinary colloidal solutions, and observations were confined to samples of these gamboge suspensions of very small depth. "Successful observations with the emulsions I have used cannot be made through heights of several centimetres or even millimetres; heights of less than a tenth of a millimetre only are suitable" (3).

Whether so intended by Perrin or not, this formula has been taken to hold for all colloidal solutions and for all depths. A little consideration will contradict the possibility of such an extension of Perrin's work.

For example, in a silver colloidal solution worked with by one of us (4), the value of P in the above formula would be given by substituting as follows in (2):—

$$\frac{RT}{N} = (\text{approx.}) 4 \times 10^{-14}, \quad \rho_1 - \rho_2 = 9.5,$$

$$V = 22 \times 10^{-15}, \quad g = 980,$$

from which

$$P = (\text{approx.}) 5000.$$

The ratio of the concentrations at any two levels 1 cm. apart would be given by the equation

$$\log \frac{n_1}{n_2} = 5000,$$

which is a result quite out of all reason, to one familiar with such solutions.

## II. *Experimental Work.*

If there is any remarkable variation in the distribution of the particles in an ordinary colloidal solution, it should be shown by allowing the solution to stand in a long vertical tube for some time.

A glass tube, 3 cm. in diameter and 94 cm. in length, has small bent glass tubes sealed on at intervals along its length and closed at the ends. This long

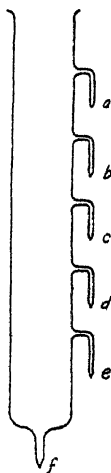


FIG. 1.

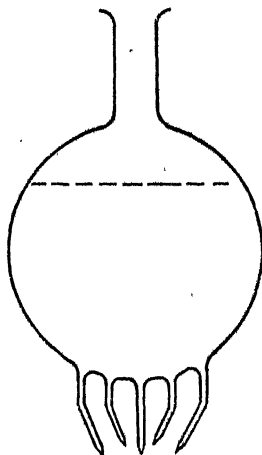


FIG. 2.

tube, after having been carefully cleaned with distilled water, was filled with copper colloidal solution of conductivity  $4.6 \times 10^{-6}$  and allowed to stand undisturbed for about fifty days in a room in which the temperature varied but little. The liquid in the different layers was then drawn off by means of the small tubes *a*, *b*, *c*, *d*, *e*, and *f*, and, after the conductivity was again measured, the liquid was evaporated and the residue weighed.

The results are tabulated below :—

Table I.

Number of layer.	Average depth from surface.	Conductivity of sample drawn off (20° C.).	Weight of copper in grm. per litre.
	cm.		
I	16.8	$7.51 \times 10^{-6}$	0.0142
II	32.0	—	0.0138
III	47.8	$6.88 \times 10^{-6}$	0.0152
IV	63.5	$6.83 \times 10^{-6}$	0.0142
V	78.8	$6.86 \times 10^{-6}$	0.0142
VI	93.8	$7.41 \times 10^{-6}$	0.0166

A slight sediment in the bottom layer accounts probably for its increased weight and conductivity. For the rest, the weight is constant within the limits of experimental error. Evidently, even if Perrin's Law holds over a small depth, a limiting concentration is soon reached, so that no difference in density is shown for considerable depths.

A similar experiment was performed, using instead of the long tube a round litre flask with five small tubes sealed in the bottom (fig. 2). This was filled with copper colloidal solution of concentration 0.242 grm. per litre and conductivity  $6.86 \times 10^{-6}$  at 20° C.

After standing about fifty days, the points of the five tubes were broken and the solution drawn slowly off into four dishes, inserted one after another. In this experiment the liquid was drawn off in layers as before, but they were less in depth and greater in area than in the previous case.

The concentrations determined were as follows:—

Table II.

Layer.	Concentration of copper in grms./litre.
I (top)	0.263
II	0.253
III	0.232
IV	0.235

This form of tube was not so well adapted to the purpose as the other, but, as before, the densities are practically constant.

To one familiar with colloidal solutions these experimental observations would have been foretold, but it remains to reconcile these results with those of Perrin on gamboge. That the concentration in such solutions tends to become uniform and is regulated by some definite properties of the particles is shown also by some experiments carried out by one of us and published some years ago (5). (See also Bancroft) (6).

“In connection with the influence of the medium the possibility of a limiting concentration is important.

“In his first paper on electrically prepared colloidal solutions, Bredig reports sols of the following concentrations:—

Platinum .....	20 mgrm. per 100 c.c.
Gold .....	14 mgrm. per 100 c.c.
Iridium .....	7 mgrm. per 100 c.c.

With the many platinum, gold, silver and copper solutions which the writer has prepared during the last few years the amount of metal per 100 c.c. has invariably been in the neighbourhood of 10 mgrm.

“The uniformity of these results points to some cause limiting the amount of metal which a given liquid will retain in the colloidal state. In order to find whether such solutions have a limiting concentration, 800 c.c. of silver

hydrosol was prepared and gradually evaporated. At the beginning and at each successive stage at which the volume of the liquid evaporated reached a half value, the amount of metal per cubic centimetre, the mobility of the particles, and the size of the particles were determined; the results of these observations are recorded in Table III:—

Table III.

Concentrated to	Weight of Ag per 100 c.c.	No. of particles per c.c.	Volume of a single particle.	Mobility constant $V \times 10^{-8}$ .
Original vol. ....	mgram. 6.2	$2.9 \times 10^8$	$2.0 \times 10^{-14}$	25.2
0.5 original vol. ...	8.8	$4.2 \times 10^8$	$2.0 \times 10^{-14}$	23.5
0.25 " " ...	10.2	—	—	23.1
0.15 " " ...	12.3	—	—	—

"It will be seen that the size of the particles and their mobility is apparently not affected by the concentration of the solution. The variation in the amount of metal per 100 c.c. as the water was extracted from the sol is illustrated in the curve in fig. 3, in which the amount of metal per 100 c.c. at any time is plotted against the concentration if all the metal had remained in suspension. This indicates strongly that there is a limit to the quantity of colloidal silver possible in water, at about 13 mgrm. per 100 c.c.

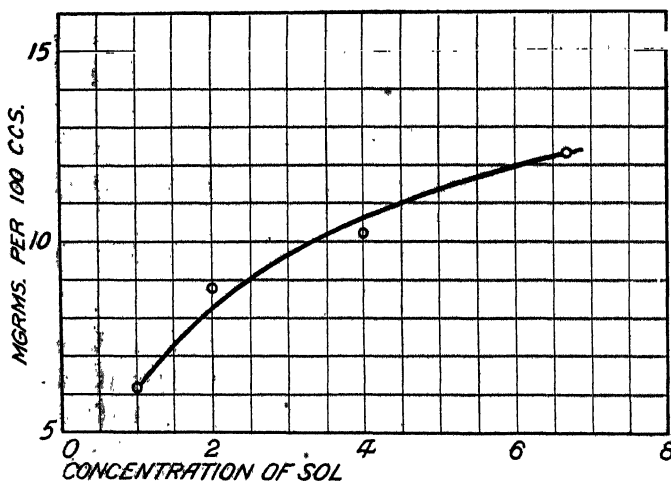


FIG. 3.

"In order to obviate any irregularity that might be introduced by heating the solution, the evaporation was carried on over sulphuric acid and calcium chloride at very low pressure, an operation extending over about a week.

"As this particular solution had been standing undisturbed and unchanged for a month before the evaporation was begun, the apparent settling of the metal is not due merely to the lapse of time. Again, it cannot be due to the concentration of electrolytic impurities in the sol, because these were not sufficient to have any appreciable effect, as is shown by the mobility determination for the first three samples." (5)

The only conclusion that can be drawn from these experiments is that fundamentally these suspensions of fine particles always reach a uniform distribution throughout the body of the liquid, and the variation expressed in Perrin's distribution law must be confined to a very small distance at the surface.

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- (6) Bancroft, 'Jour. of Phys. Chem.,' vol. 18, p. 558 (1914).

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*A New Form of Interferometer.*

By H. P. WARAN, M.A. (Madras), Government of India Scholar of the  
University of Madras.

(Communicated by Prof. H. F. Newall, F.R.S. Received November 11, 1921.)

The Lummer and Gehrke interferometer consists of a thin plate of glass with its two surfaces worked optically true and paralalled to one another. High accuracy is required in the plane parallelism, and the flatness of surface and the difficulty of working such long plates for high resolving powers, and the cost involved, sets a limit to our achievement in this direction. Such plates, even when finished, furnish results which have given rise to a considerable amount of discussion and raise doubt as to whether the appearances are trustworthy at such high resolving powers and whether they are not partly due to ghosts formed by the defects in the glass. Hence the present attempt to devise a parallel plate that would meet these objections and serve as an instrument of resolving power and precision sufficient to extend our

knowledge of the constitution of spectrum lines, and a variety of other phenomena requiring the aid of very high resolving power.

The late Lord Rayleigh\* used the free surface of a sheet of water as a true optical flat for testing plane surfaces, and describes the results of observations of interference with large differences of path between two interfering beams in a thick slab of water floating on mercury. The optical flatness of the surface of a liquid at rest suggests that, by floating a layer of water or other transparent liquid over another, like mercury, with which it does not mix, we can get an optically perfect plane parallel plate, of any length and thickness, which may be used as a parallel-plate interferometer. The following is a brief account of the results of a series of experiments, conducted under great experimental difficulties during 1918-1919, to test the practicability of this idea.

The light used was that of a glass mercury-vapour lamp, filtered through a green filter to get the intense monochromatic radiations of wave-length  $5460.7 \text{ \AA.U.}$  Analysis of the light transmitted by this filter showed that the two yellow lines were still present faintly, while the other lines were practically eliminated. Lamps of convenient form were successfully constructed by the writer.

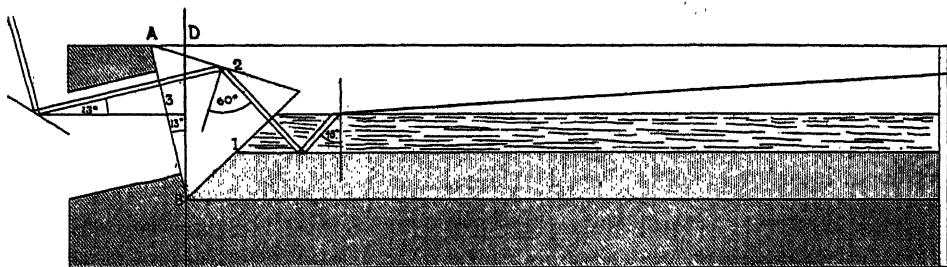
The first experiments were made with a layer of water about 1 cm. deep, floating on mercury. The collimated light, entering the water surface normally, was reflected by an adjustable mirror mounted in the liquid, so as to be incident on the upper surface at the proper angle to ensure a large number of reflections within the layer. The emergent beams of rays were caught in a telescope and examined for the formation of the system of interference bands.

To eliminate troubles arising from tremors on the surface of the water, the experiments were made in the basement cellar of the laboratory at Madras. The apparatus was enclosed in a case to exclude draughts, and the trough was mounted on elastic cushions, placed over a specially designed massive platform resting on rubber corks. But still the water surface was not quiet enough for the purpose in view. When a layer of clear castor oil was used, the surface was found to be more steady, but yet the bands were not visible, though the optical conditions appeared to be satisfied. Further consideration showed, however, that the reflections at the lower and the upper surfaces of the liquid were taking place under such different conditions that the formation of a sharp system of bands was not to be expected, unless the light was polarised in or perpendicular to the plane of incidence. When a nicol prism, suitably orientated, was interposed in the path of the light, the bands

\* 'Collected Papers,' vol. 4, p. 56.

became clearly visible. The surface was found to be much more steady in the quiet hours of the morning, and with short exposures it was found possible to photograph the fringes. The poor transparency of castor oil, however, made high resolving power unattainable. After a good deal of further experimentation, means were devised to overcome the disturbing effects of the surface tremors of the ground, efficient enough to make the employment of a layer of water possible, and a mount was designed to carry the trough containing the liquids which would not communicate the surface tremors of the ground. The final arrangement consists of a brick pillar built on a massive foundation considerably beneath the level of the ground in the cellar, the stone slabs forming the floor not being in contact with the pillar. On the top of this pillar rests a massive porcelain trough, containing water in which floats a platform that is prevented from coming into contact with the sides of the porcelain trough. This platform carries a massive levelling table, supported on rubber corks and covered with a few layers of felt. On the top of the felt the trough carrying the liquids is placed. Thin copper wires, attached to the platform, and led over small pulleys on the ceiling to a keyboard on the pillar, serve to steady the platform. By turning the keys these wires may be kept taut, and the platform, floating with a certain amount of constraint, behaves as a massive pendulum with its bob partly immersed in the water.

The trough, which contains the interferometer liquids, is a closed rectangular vessel,  $40 \times 10 \times 6$  cm. in size. One end is formed by a prism of equilateral section, attached to the sides of the trough, with one of its surfaces inclined at an angle of  $13^\circ$  (for water) to the vertical, as shown in the figure. The collimated beam, which is reflected upwards, enters the first



face of the prism normally, and after total reflection at the second face enters the liquid after passing out normal to the third face. This arrangement effects a considerable saving in light and is very convenient in practice. To prevent stray light in the field of the telescope, caused by the capillary curvatures of the liquid in contact with the prism, a wide slit with adjustable



jaws is mounted in front of the aperture in the trough and restricts the collimated beam to a suitable width in the central region. The trough is completely enclosed, to prevent the disturbing effects of air currents, and the emergent light passes out through a thin mica window on the end opposite to the prism.

With this arrangement experiments were made successfully with a layer of water resting on mercury. During the daytime the heavy traffic in the near neighbourhood of the laboratory and the movement of students were disturbing. But during the quieter hours of the night the fringes were found to be remarkably steady notwithstanding the disturbing effect of the sea waves, 300 yards away. The fringes are found to be remarkably sharp on quiet days. The success of the arrangement has been proved beyond a doubt and, notwithstanding its complexity in its present form, its advantages over the glass plate are evident.

The resolving power  $R$  of a parallel plate may be expressed\* as

$$R = 2\mu tn \cos r,$$

where  $\mu$  is the refractive index for the wave-length used,  
 $t$  is the thickness,  
 $r$  is the critical angle,  
 and  $n$  the number of emergent beams.

But 
$$n = \frac{L}{2t} \cot r,$$

where  $L$  is the length of the plate; and

$$\mu = \frac{1}{\sin r}. \quad \text{Hence } R = L \cot^2 r,$$

*i.e.*, the resolving power is directly proportional to the length. Thus for securing high resolving powers we may use the maximum length which the quantity of light and the transparency of the liquid will permit. The above relation shows that the resolving power is independent of the thickness.

Further, in a system of interference bands formed by a parallel plate, the order of interference  $N$  is given by the relation

$$N = \frac{2\mu t \cos r}{\lambda},$$

where  $\lambda$  is the wave-length of light in question. Differentiating, we get

$$dN = -\frac{2\mu}{\lambda} t \sin r \, dr,$$

\* The elementary theory given here is recognised as inadequate, and my attention has been called to the detailed theory given in Gehrcke's book, 'Anwendung der Interferenzen,' 1906, and Kolacek's paper in 'Ann. der Phys.,' vol. 39, p. 1431 (1912).

and for two thicknesses of glass  $t_1$  and  $t_2$  we get the two relations

$$\frac{dN_1}{dr_1} = -\frac{2\mu}{\lambda} t_1 \sin r$$

and

$$\frac{dN_2}{dr_2} = -\frac{2\mu}{\lambda} t_2 \sin r.$$

Therefore  $\frac{dN_1}{dr_1} / \frac{dN_2}{dr_2} = \frac{dr_2}{dr_1} = \frac{t_1}{t_2}$  since  $dN_1 = dN_2 = 1$ .

But  $\frac{\sin i}{\sin r} = \mu > 1$ ,

where  $i$  is the angle of emergence corresponding to the angle of refraction  $r$ .

Therefore, the corresponding  $di_2/di_1$  which expresses the ratio of the separation between the two lowest order bands in the two cases is given by the relation

$$\frac{di_2}{di_1} = k \frac{t_1}{t_2},$$

where  $k$  is some factor of numerical value greater than unity.

This shows that the thickness of the plate affects the separation between the individual bands in the interference pattern, and it is seen that the separation varies inversely as the thickness of the plates forming them. In practice it is advantageous to have the individual bands widely separated to secure high resolving powers and hence the thinner the plate the better. But with glass for purposes of mechanical strength and rigidity the thickness for a given length cannot be reduced beyond a certain limit, while with the liquid plate the need for such limitation does not enter. In fact it is found in practice that the liquid plate gets steadier the thinner it is. The limit is then set by the curvature due to capillarity. The greater the amount of light that can be introduced into the plate the stronger the multiple reflections and the sharper and brighter the fringes. If the amount of light introduced into the plate be increased by increasing the thickness, the decreased separation between the fringes is disadvantageous. It is preferable to introduce more light into a plate by increasing its width, a course obviously less costly in the case of a layer of water than in the case of optically worked glass.

Considered in all these aspects, notwithstanding the complexity of the suspension, its advantages are clear and doubtless the arrangements can be further simplified.

In conclusion I must express my indebtedness to Prof. R. Ll. Jones, of the Presidency College, Madras, for his kind and sympathetic help in the prosecution of this research.

*On the Whispering-Gallery Phenomenon.*

By C. V. RAMAN, M.A., Palit Professor of Physics in the Calcutta University,  
and G. A. SUTHERLAND, M.A., Assistant Lecturer in Physics, University  
College, London.

(Communicated by Prof. A. W. Porter, F.R.S. Received September 6, 1921.)

1. *Introduction.*

The theory of the curious and interesting effects observed in the Whispering Gallery at the base of the dome in St. Paul's Cathedral was discussed long ago by the late Lord Rayleigh in his treatise on Sound,\* and more fully, from the point of view of wave-propagation, in two recent papers.† Expressed in general terms, the explanation put forward is: the sound-waves cling to the concave surface of the wall and travel circumferentially along it, suffering a diminution of intensity relatively small in comparison with that of waves spherically diverging from the source. The theory was supported by the observation that the effects under consideration are most noticeable when a *directed* source of sound is used and placed close to the curved surface, with its maximum emission in a direction tangential to it. An experimental illustration of the theory was also put forward,‡ using a semicircular reflector of sheet metal, with a bird-call as a source of sound of short wave-length, and a high-pressure sensitive flame as detector. With this apparatus, a small obstacle placed close to the concave surface is competent to intercept most of the effect. Some recent experiments of Barton and Kilby,§ illustrating the matter further, by the aid of dust-figures produced by electric sparks, may also be mentioned.

On account of the great interest of the subject, not only from a purely acoustical standpoint, but also in view of analogous effects in other branches of physics, *e.g.*, the propagation of electric or seismic waves round the earth, it occurred to the authors that it would be worth while to make a closer investigation of the phenomena and of the explanations that have been advanced, and this paper describes the results obtained.

\* Vol. 2, 2nd edition, pp. 126-128.

† 'Phil. Mag.,' vol. 20, p. 1001 (1910); 'Scientific Papers,' vol. 5, p. 617; 'Phil. Mag.,' vol. 27, p. 100 (1914); 'Scientific Papers,' vol. 6.

‡ 'Roy. Inst. Proc.,' January, 1904; 'Scientific Papers,' vol. 5, p. 171; see also Sir William Bragg's 'The World of Sound,' pp. 84-86.

§ 'Phil. Mag.,' vol. 24 (1912).

*2. The Optical Analogue of the Whispering-Gallery Effect.*

In view of the remark by Rayleigh in a footnote to his paper, as reprinted in his collected works,\* that his theory should be applicable equally for electro-magnetic waves, as in the case of sound, it will be appropriate here to refer to the results of some observations on the curvilinear propagation of light along a reflecting surface, initiated by one of us (C. V. R.), and carried out by Mr. Bidhubhusan Ray at Calcutta. The experiment was intended to find how the effect due to a light-source placed on a reflector alters with the curvature of the surface. It was carried out in the following way. A strip of plane mirror, about 100 cm. in length and 5 cm. broad, rested on two wooden supports near its ends. A razor edge, placed on the mirror near one end, formed an exceedingly fine slit between it and the surface on which the light of a mercury lamp with green ray filter was concentrated. Two light wooden bridges, placed on the mirror near its two ends, and equally loaded, enabled a curvature of variable magnitude to be imposed on the mirror. It was very interesting to watch the luminous effect at the distant end of the mirror through an eyepiece as the curvature was gradually increased. When the surface was quite plane, there was only a very faint general illumination of the field, the edge of the mirror being, however, a perfectly black line. When a slight curvature is put on, there is a very rapid increase in the luminosity of the field, a bright band of light flashing out next to the surface of the mirror, which continues to be seen as a line of zero illumination. With further increase of curvature this band contracts in width, and is followed by a second bright band, separated from it by a dark band. Then a third bright band appears, preceded by another dark band, and so on, the number of bands and their sharpness increasing, and their width decreasing with the increase in the curvature of the mirror. More and more light is heaped up, as it were, near the surface of the mirror. Some striking differences also appear in the intensity of the different bands, and ultimately also in their spacing, and it then becomes possible to differentiate the head of the caustic formed by a single reflection at the surface of the mirror from the train of feebler and narrower bands following it, in which also appear variations of intensity, which might be interpreted as due to the superposition of caustics of second and higher orders.

According to Rayleigh's theory, the light vector in the experiments described above should be zero on the surface of the mirror, and on moving away from it should increase to a maximum and then decrease again rapidly, remaining very small for all further displacements. As we have seen above,

\* 'Scientific Papers,' vol. 5, p. 617.

this agrees with what is observed when the radius of curvature of the mirror is exceedingly large (practically infinite) in comparison with the wave-length of light, and with a smaller radius we get not merely a single maximum adjacent to the surface, but several such maxima, separated from each other by intervening minima. Accepting this as a guide, we see that in the acoustical case, where the radius of the reflecting surface is a relatively modest multiple of the wave-length, we should get, not a single narrow belt of maximum intensity skirting the wall of the gallery, but several belts of sound alternating with silence.

### 3. *Observations in St. Paul's Cathedral and in the Laboratory.*

By courtesy of the authorities of St. Paul's Cathedral we have been enabled to carry out some observations in the Whispering Gallery. Owing to the limitations of time, there was not sufficient opportunity to make any reliable *quantitative* observations in the gallery, but as to the general nature of the phenomena observable in it, there was no doubt whatsoever. With a steady source of sound placed on the wall of the gallery at one point and blown from a bellows at steady pressure, observations were made at different points in the gallery. Exceedingly well-marked fluctuations of intensity were perceptible as the observer's ear was moved radially away from the wall, sound alternating with comparative silence at distances of the same order as the wave-length of the sound. (At the minima, some of the overtones of the source could be heard while the fundamental was practically silent). These radial fluctuations of intensity could be observed practically at all points in the gallery. Very pronounced fluctuations of intensity were also noticeable when the observer's head was moved *circumferentially*, that is, parallel to the wall, and this latter effect, though detectable everywhere, was most marked near the far end of the diameter of the gallery in which the source was situated. The distances apart of the successive minima were about half the wave-length of the sound used. It was found that by using a fairly high-pitched source of sound and a sensitive flame run from a cylinder of gas under pressure, the radial and circumferential fluctuations of intensity could be demonstrated in the gallery.

It was found also that similar effects could be observed in the laboratory, using a bird-call or a Galton whistle, blown from a steady-pressure bellows as source, and a sensitive flame as detector, with a curved metal sheet as the reflecting wall. In one series of observations, a semicircular archway at the University College Laboratory was also successfully used to exhibit the effect. We should here mention an important difference which was noticed between the case in which a semicircular reflector is used and that of a complete

circular reflector. It is obvious that in the latter case the sound can go right round the circumference in either direction, whereas in the case of the semicircular cylinder we are confined to the effects due to the propagation of sound in one direction only. In both cases radial and circumferential variations of intensity may be observed; but their character, *especially of the latter*, is different in the two cases. It was found in the case of the semicircular reflector that the circumferential variations of intensity did not occur at equidistant points, but were much more crowded together near the end of the diameter remote from the source. With the complete circular reflector, on the other hand, they were equidistant, suggesting thereby that the circumferential nodes and loops in the latter case were due mainly to the interference of waves travelling in opposite directions along the surface of the gallery.

#### 4. Discussion of the Theory.

Rayleigh's theory is attractive in its simplicity, but as is evident from the foregoing experimental results, it does not fully explain the observed phenomena. The treatment is based on the assumption that the progressive wave can be represented by a term of which the amplitude factor is a Bessel function\* of large integral order which vanishes *only* on the boundary, but *not* also at any internal points; in other words, that it is analogous to a stationary vibration with a large number of nodal diameters but no internal nodal circles. This assumption would be justifiable if the wave-motion were *strictly* circumferential, but in the actual circumstances of the problem this is not rigorously true, as a certain amount of divergence in the radiation from the source is inevitable. In attempting to develop a more complete theory, two distinct modes of approach suggest themselves, neither of which, however, is free from difficulties. The first method is to regard the illumination near the surface of the mirror as due to the superposition of the fringe-systems accompanying the caustics formed by one, two or more reflections, utilizing Airy's well-known investigation for the purpose. The second method is to treat the progressive disturbance as the resultant of two systems of stationary waves differing in phase existing in the space enclosed by the cylindrical wall, and to investigate the latter by the method of stationary vibrations on the basis of the strict dynamical theory and of the boundary conditions to be satisfied at the surface of the wall. Perhaps the difference between the two methods of approach here indicated is really less fundamental than might seem at first sight, for as has been shown by J. W. Nicholson, the Bessel functions of large but nearly equal order and argument involved in the solution of the

\* Or its differential in the case of the velocity potential in the acoustical problem, and of the magnetic vector in the electromagnetic problem.

boundary-value problem are most easily evaluated by transforming them into integrals of Airy's type. The important point to be noticed is that the solution on the basis of strict dynamical theory would include vibrations having nodal *circles* as well as nodal *diameters*. Either mode of dealing with the problem thus indicates *radial* alternations of intensity of the kind observed in experiment. The *circumferential* alternations of intensity would arise in two ways: (a) by the superposition of progressive waves travelling in opposite directions round the gallery; and (b) by the superposition of progressive waves of identical frequency travelling in the same direction but of slightly differing *circumferential* wave-length, that is, having a larger or smaller number of *nodal circles*. The effect contemplated in (a) necessarily arises when we are dealing with sustained sounds in a circular gallery and may be regarded as simply representing a modified type of stationary vibration. The effect in (b) is most easily observed in experiments with a semi-circular gallery, as it then occurs by itself.

#### 5. Summary and Conclusion.

The paper deals with some observations made in the Whispering-Gallery in St. Paul's Cathedral and also in laboratory experiments, which show that while Rayleigh's theory of the phenomenon is undoubtedly on the right lines, it does not offer a complete explanation of all that is observed. The optical analogue of the Whispering-Gallery is described, and it is shown that the effect contemplated by Rayleigh, that is, a single belt of maximum intensity close to the wall, is obtained only in the limiting case when the radius of the reflecting circle is practically infinite in comparison with the wave-length. For more moderate values of the radius of curvature, we get a succession of belts of alternately great and small intensity. Similar effects are also observed in the acoustical case. The explanation of the results is discussed, and it is shown that the slight inevitable deviation from the condition of strictly circumferential wave-propagation postulated by Rayleigh must give rise to such effects.

A considerable part of the experimental work described in this paper was carried out at University College, London, during the short visit of one of us to England. We wish to express our cordial thanks to Prof. A. W. Porter, F.R.S., for his kindly interest and encouragement and for the facilities he put at our disposal for the investigation.

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## *On the Viscosities of the Hydrogen Halides.*

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The measure of agreement between the values of the atomic diameter obtained from W. L. Bragg's crystal measurements, and those deduced from viscosity data and the Kinetic Theory, has recently been demonstrated by A. O. Rankine\* for the halogen gas molecules, in which the two atoms are of equal size. The mathematical treatment by which the mean collision area is obtained, can be extended to molecules compounded of two unequal atoms such as those of the hydrogen halides, and the present viscosity experiments were undertaken with a view to affording a test of the further theoretical investigation of Prof. Rankine.†

### *General Method of Procedure.*

The chemical activity of these gases limits the possible modes of measuring the viscosity, and is the cause of the chief difficulties of the experiments. The method chosen was that of the transpiration of the gases through a capillary tube, the dimensions of which were obtained by transpiring air. The viscosity of air is now sufficiently well known to justify its use for this purpose, and the uncertain measurements of the length and diameter of the tube are thus avoided.

The purified gases were first liquefied, and then enclosed and allowed to evaporate. The process of evaporation could be controlled so as to establish a suitable driving pressure, the pressure difference between the ends of the capillary being observed on a liquid U-tube gauge. The masses of gas passing were measured by absorbing in water and titrating with standard alkali. The corresponding volumes were obtained from density data.

Experiments were performed at two temperatures, the interval being about 85° C. This enables Sutherland's constant to be calculated for these

### *Determination of the Constant of the Tube.*

The capillary tube was selected from many that were calibrated. That ultimately chosen was 80 cm. in length, the maximum variation being less than  $\frac{1}{2}$  per cent. of the mean diameter, which was 0.0342 cm. (found by

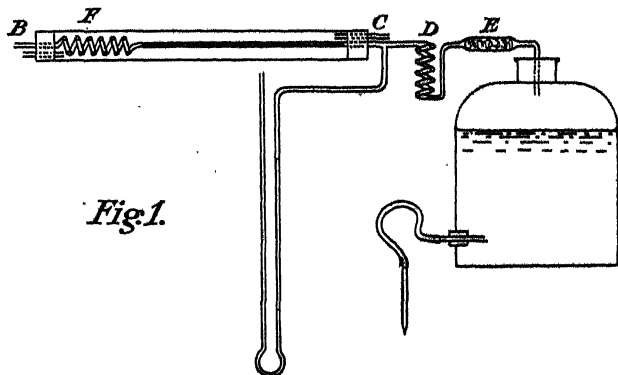
\* 'Roy. Soc. Proc.,' A, vol. 98, p. 360.

† 'Phys. Soc. Proc.,' June, 1921.



weighing a thread of mercury filling this length). The order of diameter suitable for the proposed method of establishing the pressure difference was previously ascertained by trial with various tubes.

The form of the apparatus is shown diagrammatically in fig. 1. Air is drawn through the capillary tube by means of an aspirator, the volume of



*Fig. 1.*

water run off giving, after several corrections, the volume of air passing. The end B is open to the atmosphere through drying tubes containing (1) calcium chloride and soda-lime; (2) phosphorus pentoxide; and (3) glass-wool. The spiral F, made of about a metre of 5-mm. tubing, sealed on to the experimental tube and enclosed in the same jacket, ensures that the air enters the capillary at the temperature of the jacket, at least for the rates of flow used, which amounted to only a few cubic centimetres per minute. The pressure difference is read on a sulphuric acid gauge, one limb of which was connected at C, while the other is open to the atmosphere. The density of the acid was found, and conveniently checked from time to time by comparison with a distilled water gauge, placed temporarily in parallel at the four-way piece, C. As a mean of seven readings at various pressure differences, the value found was  $1.840 \pm 0.0004$  times the density of water in the neighbourhood of  $20^{\circ}\text{C}$ .

As the aspirator was at room temperature (usually above the temperature of the jacket), the spiral D was inserted and kept immersed in a beaker of water at room temperature. The tube E contains calcium chloride, to protect the capillary tube from water vapour drawing back. The aspirator had an area of cross-section of about 700 square cm., so that the pressure head varied but slightly during a collection lasting, say, 15 minutes. Variations in the pressure head were conveniently made between wide limits, without necessitating a very large aspirator, by varying the height of a nozzle attached by pressure tubing to the exit tube.

Meyer's transpiration formula,

$$P_1 V_1 = P_2 V_2 = \frac{(P_1^2 - P_2^2) \pi a^4}{16 l \eta},$$

can be written

$$\eta = \frac{(P_1 - P_2)(P_1 + P_2)}{16 l P_2 V_2} = \frac{\delta(2P_1 - \delta)}{(P_1 - \delta) V_2} \frac{60 g \rho_0 \pi a^4}{16 l},$$

where  $\delta$  = pressure difference (obtained from gauge readings).

$P_1$  = atmospheric pressure =  $P_2 + \delta$ , all measured in centimetres of mercury at  $0^\circ$  C., and  $\rho_0$  = density of mercury at  $0^\circ$  C.

$V_2$  = volume of dry air passing per minute at pressure,  $P_2$ , and temperature of the jacket,  $t_c$ .

In the experiments, the volume of water collected gives the increase in the volume of saturated air in the aspirator, at pressure  $P_2$ , and temperature,  $t_a$ . Two corrections have therefore to be applied. Volume  $V_2$ , on entering the aspirator, is raised from  $t_c$  to  $t_a$ . Further, it has become saturated (this assumption is probably correct for the small rates of flow used). Since the total pressure,  $P_2$ , remains constant, the partial pressure of the air in the aspirator is less than  $P_2$  by the saturation vapour pressure of water at  $t_a$ , and the air accordingly expands, so that if  $V$  = observed volume of water displaced per minute, after correction for the temperature,

$$V_2 = \frac{P_2 - \sigma}{P_2} V = \frac{P_1 + \delta - \sigma}{P_1 - \delta} V.$$

Substituting in the equation for  $\eta$ ,

$$\eta = \frac{60 g \rho_0 \cdot \pi a^4}{16 l} \cdot \frac{\delta(2P_1 - \delta)}{(P_1 - \delta - \sigma)V} = K \frac{\delta(2P_1 - \delta)}{(P_1 - \delta - \sigma)V}$$

where  $K$  contains all constant quantities, so that if  $\delta$ ,  $P_1$  and  $\sigma$  are in centimetres of mercury at  $0^\circ$  C.,  $V$  in cubic centimetres per minute at  $P_2$  and  $t_c$ , the equation gives the viscosity. The values of  $\eta_{\text{air}}$ , used in calculating  $K$ , are the most recent of Prof. Rankine, viz.,

$$\eta_0 = 1.724 \times 10^{-4} \text{ C.G.S. units,}$$

$$\eta_{15} = 1.799 \times 10^{-4} \quad ,,$$

In setting up the apparatus for the determination of  $K$ , glass joints were made throughout (except the connection to the aspirator, which, however, was well waxed) to prevent leak. A preliminary experiment was made to ascertain the limit of steady flow before turbulence sets in for the tube in use. We have

$$V_2 \propto \delta \frac{(2P_1 - \delta)}{P_1 - \delta},$$

i.e., 
$$V_2 \propto 2\delta \left(1 + \frac{\delta}{2P_1}\right) \text{ approximately.}$$

It was found that, up to about 60 cm. sulphuric acid, the values of  $V_2$ , plotted against  $\delta(1 + \delta/2P_1)$ , gave a straight line, showing that the condition of steady flow obtained.

Several sets of determinations of  $K$  were made during the course of the experiments upon the gases, varying the pressure difference over the range from 10 to 40 cm. sulphuric acid. The constancy of  $K$  throughout showed that it was independent of the set-up of the apparatus, and therefore that there was no leak, and at the same time confirms that the region of velocities used was that of steady flow.

The temperature of the jacket was maintained constant by passing a rapid stream of water through it, and was recorded as the mean of the inlet and outlet temperatures, measured with mercurial thermometers graduated in  $1/10^\circ \text{C}$ . A third thermometer, suspended within the aspirator, gave  $t_a$ . All three were compared with a standard thermometer which had been recently calibrated, and their lower fixed points were checked.

The volume of water collected in a known time was found by weighing, correcting for buoyancy and the density of water. The times were measured with a stop-watch, which was used throughout the experiments.

The disadvantage of this method of determining  $K$  is that variation in temperature of the aspirator during an experiment will affect the volume of water collected. The error was minimised by wrapping the aspirator in cotton-wool and leaving it for some hours after setting up, in order that a steady temperature might be reached before beginning the measurements. The temperature was then taken at intervals and the pressure difference also observed, the means being used in the calculations.

Table I.

$t^\circ \text{C}$ .	$K \times 10^4$ .	$t^\circ \text{C}$ .	$K \times 10^4$ .	$t^\circ \text{C}$ .	$K \times 10^4$ .
10.0	1.7076 1.7044 1.7077 1.7078 1.7028	9.5	1.7073 1.7088 1.7085	19.0	1.7087 1.7045 1.7116 1.7117 1.7064
Means .....	1.7080		1.7084		1.7080

Table I records the values of  $K$  obtained in three sets of experiments, taken before and after the HCl experiments, and with bromo-naphthalene in the gauge preparatory to the HBr experiments.

At steam temperature  $K$  will have a slightly increased value, on account of

the expansion of the capillary. This has been deduced by assuming the coefficient of linear expansion of glass to be 0.000009.

The mean value of  $K_{19}$  is  $1.7076 \pm 0.00005 \times 10^{-4}$ . As a check upon this figure, the value of  $K$  was also calculated from the dimensions of the tube.

Approximate length of capillary = 78.4 cm.

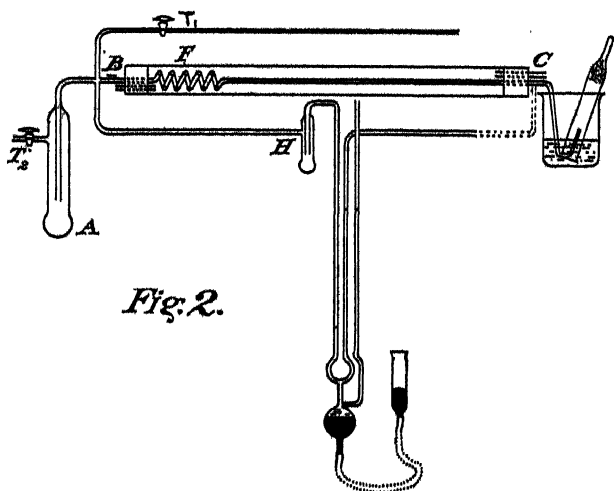
„ diameter „ = 0.0342 cm.

The value thus obtained was  $K = 1.705 \times 10^{-4}$ , and the agreement to 0.15 per cent. is satisfactory.

### *Hydrogen Chloride.—Description of Apparatus.*

The apparatus used for the viscosity of hydrogen chloride is shown in fig. 2. The gas was prepared by dropping concentrated sulphuric acid on pure sodium chloride, and was dried by passing over  $P_2O_5$  in a metre length of  $\frac{1}{2}$ -inch tubing, entering the apparatus at tap  $T_2$ . After having displaced air from the apparatus, the bulb A was surrounded by liquid air, the flask being lowered occasionally to allow the solid HCl to liquefy and collect in the bulb.

The form of the pressure gauge designed for these experiments is clear from fig. 2. The U is connected below to a bulb, and then by flexible tubing



to a mercury reservoir. The gauge liquid (sulphuric acid for HCl) rests on mercury, and by raising or lowering the reservoir can be made to stand at any point in the gauge tubes; or it can be lowered beyond the U, so that air can be swept from the connecting tubes.

The gauge was originally connected at B and C, while the third limb shown

was open to the atmosphere; but with the method of collection described below, this third limb indicated that connection to C was unnecessary, as the pressure there remained atmospheric. The trap H was added to prevent the gauge liquid from being drawn back into the apparatus with the sudden variations of pressure when liquefying the gas. It was found convenient to have the capillary and tap  $T_1$  closed, with a few centimetres of liquid in the U of the gauge; this indicated the variations of pressure and made it possible to generate the gas at such a rate that practically all was liquefied.

An auxiliary capillary tube was connected at B in parallel with the experimental one through tap  $T_1$ . Its inclusion gives a ready means of varying the pressure difference across BC by altering the length in circuit. This arrangement works more satisfactorily than a tap.

When the steady pressure difference is established (see later), a means is required of absorbing the gas in water for a definite time and which will not disturb the pressure at C. The following simple arrangement was proved to satisfy both conditions. The exit tube is drawn out and bent as shown; at the required moment a test-tube, drawn out and open to the atmosphere at its upper end through a plug of moistened glass wool, was clapped over the nozzle and at the same moment a beaker of water was brought up into position from below. Moistened blue litmus-paper placed upon the open end of the test-tube showed that no gas escaped beyond the glass wool. At the end of the required time the test-tube was raised and the beaker lowered simultaneously, and with the exit nozzle shaped as shown, very little water adhered to it. The acid from the test-tube was washed into the beaker and the whole acid titrated with N/10 KOH, using phenol phthalein as indicator, or N/10  $\text{Na}_2\text{CO}_3$ , using methyl orange.

#### *The Viscosity Experiment.*

When about 10–15 c.c. of liquid HCl had condensed in the bulb A, the tap  $T_2$  was closed and the generating apparatus removed. The liquid air flask was lowered until sufficient gas had passed over to sweep all air from the apparatus, the gauge liquid being lowered to clear its tubes and then raised to send a rapid current of gas through the capillaries. The bulb A was then surrounded by an empty Dewar flask and the whole heavily wrapped in cotton wool. It was found that the rate at which the gas evaporated from the liquid HCl soon settled down to a constant and measurable value, depending on the small amount of heat reaching the bulb. By varying the length of the auxiliary capillary tube in parallel with the experimental one, the pressure differences between B and C could be reduced to any desired value suitable for a viscosity measurement. This pressure difference remained

remarkably steady and only varied gradually, usually by less than 1 per cent., during the 10-20 minutes taken for an experiment. During the initial stages, however, sudden fluctuations of several per cent. occasionally occurred, perhaps as bubbles of gas rose to the surface in bulb A. This was noticed more particularly at the lower temperature experiments. By observing the pressure difference every 2 minutes, the mean value is obtained in which these variations are unimportant.

Several series of experiments were made at the temperature of the water supply and at steam temperature, varying the pressure difference, but keeping well within the limits of steady flow for air. When the time of collection of the gas was varied; no systematic error due to end-effects could be detected. The initial and final portions of gas coming over from A were neglected as possibly containing impurity. A test of the purity of the gas was made by collecting a sample over dry mercury; when a little water was inserted, the whole of the gas dissolved.

The transpiration formula in this case gives

$$\eta_t = K_t \frac{(P_1 - P_2)(P_1 + P_2)}{P_2 V_2} = K_t \frac{\delta(2P_2 + \delta)}{P_2 V_2}$$

where

$$P_2 = \text{atmospheric pressure} = P_1 - \delta.$$

As before,  $P_2$  and  $\delta$  are converted to centimetres of mercury at  $0^\circ \text{C}$ . The appropriate value of the constant is obtained from the experimental value, using the formula

$$K_t = K_0 (1 + 3\gamma t) \quad \text{where} \quad \gamma = 0.000009.$$

The volume of gas ( $V_2$ ) at pressure  $P_2$  and the temperature of the jacket is calculated from the weight of gas deduced from the titration results; and here enters probably the greatest error of the method. For the molecular weight density is certainly too low, owing to slight departures from perfect gas laws even at ordinary temperatures. The experimental density at  $0^\circ \text{C.}$  as given by Guye and Gazarian (Kaye and Laby's Tables) is therefore assumed, and the constants of Van der Waal's equation (Dewar, 1884) used to obtain the density at the required temperatures, this being considered the best approximation available. The data used are:—

Experimental density at 0° C. and 760 mm. = .16399 grm. per litre.

Van der Waal's constant,  $a$  = 0.00697,
$$b = 0.00173.$$

The volume of gas ( $v$ ) under pressure  $P_2$  and at the jacket temperature  $t_c$  equivalent to 1000 c.c. N/10 solution is the quantity entering directly in the

calculation of  $\eta$  and the values used for the two sets of experiments recorded in Table II are given below :—

At 12.5° C. and 759.6 mm.,  $v = 2326$  c.c. per litre.

At 100.3° C. and 768.8 mm.,  $v = 3014$  „

(The molecular weight values are 2343 c.c. and 3026 c.c. respectively.)

The means of the sets of viscosity results at 12.5° C. and 100.3° C. recorded in Table II are used to calculate Sutherland's constant  $C$ , from the expression,

$$\frac{\eta_2}{\eta_1} = \left(\frac{T_2}{T_1}\right)^{3/2} \left(\frac{C+T_1}{C+T_2}\right).$$

Table II.

$t$ ° C.	$\eta \times 10^4$ .	$t$ ° C.	$\eta \times 10^4$ .	Sutherland's constant $C$ .
12.5	1.398 1.385 1.399 1.373 1.389 1.414	100.3	1.838 1.836 1.838 1.840 1.837	
Means .....	1.397 $\pm 0.003$		1.838 $\pm 0.0004$	357

The method has the advantage that a steady continuous flow is attained which allows the quantities involved to be measured with considerable accuracy. The least accurate is the titration; it was convenient, however, to run the experiment for a sufficient time to collect an amount of gas equivalent to 50–60 c.c. N/10 solution, and this can be titrated to an accuracy of 0.1 c.c. or 1 part in 500; and this also seems to be the order of accuracy indicated in the final mean values of the viscosity, by application of the recognised rules for estimating probable errors.

### *Hydrogen Bromide.*

The gas was prepared by dropping bromine on a mixture of red phosphorus, sand and water, and was freed from bromine vapour by passing through a U-tube containing moist glass wool mixed with red phosphorus, drying over  $P_2O_5$  as before.

The experiment was carried out exactly as for hydrogen chloride, except that another gauge liquid was required, since sulphuric acid is attacked by HBr. Bromonaphthalene was selected as a suitable liquid for a gauge, the density being found by comparison with a water gauge in parallel. As a mean of seven readings at different pressures, the density was  $1.5175 \pm 0.003$

times the density of water in the neighbourhood of 20° C. In this case, as indeed in the previous experiment, the gas dissolves to some extent in the gauge liquid, but as the area of contact is small, the alteration in density is negligible, especially for the liquid in the further column which measures  $\delta$ .

Accurate experimental data for the density of hydrogen bromide for the calculation of  $V_2$  are not available, the only estimates being those of Biltz (1892) and Strecker (1882). The experimental measurement was, therefore, undertaken.

*Density of HBr.*

A metre length of  $\frac{3}{4}$ -inch tubing was drawn out at the ends and taps sealed on, the tube being enclosed in a jacket for water or steam. It was evacuated, connected to  $T_1$  (fig. 2), and filled with the gas prepared and liquefied as above. Both taps were then opened, and a vigorous current of gas passed over from A to sweep out last traces of air. The purity of the issuing gas was tested by collecting a sample in a large test-tube over mercury; when a little water was inserted the whole of the gas dissolved except for a minute bubble which might possibly have been hydrogen as the mercury surface was badly fouled.

When satisfied that all air had been driven out, the taps were closed leaving the pressure inside greater than atmosphere, and a stream of water was passed through the jacket until a steady temperature had been reached, when one tap was opened for a moment, gradually to avoid oscillations, thus establishing atmospheric pressure inside. One end of the tube was then opened under water, which rose owing to absorption, and the whole of the gas was carefully absorbed and washed into a beaker, titrating with N/10 KOH as in measuring the volumes in the viscosity experiments. The volume of the tube between the taps was measured by weighing the distilled water filling it and was 229.6 c.c. at 20.4° C.

In this way the density of HBr was measured at both water and steam temperatures. Though the method makes no claim as an accurate absolute determination, it at least affords a means of passing back from volumes of N/10 solution to volumes of gas, especially as the gas was prepared in the same way in both viscosity and density experiments.

The density proved to be greater than the molecular weight value, as indeed would be expected. According to Hautefeuille\* dissociation does not begin until above 700° C. The values of  $v$  deduced from the density experiments are as follows:—

At 18.7° C. and 762.2 mm.,  $v = 2370$  c.c. per litre N/10.

At 100.0° C. and 760.1 mm.,  $v = 3046$  c.c.     "     "

(The molecular weight values are 2379 c.c. and 3059 c.c. respectively.)

\* 'Compt. Rend.,' 1867.



In Table III the results of several sets of viscosity experiments are recorded, those at the lower temperature all being reduced to 18.7° C. to give the mean used in calculating Sutherland's constant C.

Table III.

$t$ °C.	$\eta_t \times 10^4$ .	$\eta_{18.7} \times 10^4$ .	$t$ °C.	$\eta_t \times 10^4$ .	Sutherland's constant C.
18.3	1.831	1.834	100.2	2.864	
17.9	1.810	1.815		2.358	
	1.838	1.843		2.365	
	1.824	1.829		2.372	
	1.829	1.834			
18.7		1.840			
		1.857			
		1.835			
		1.845			
		1.817			
18.7	Means .....	1.835 $\pm 0.0027$	100.2	2.865 $\pm 0.0019$	375

### *Hydrogen Iodide.*

The gas was prepared by dropping water on a mixture of pure re-sublimed iodine and red phosphorus, and was liquefied in bulb A after passing over red phosphorus and  $P_2O_5$  as for HBr. Some difficulty was experienced in finding a suitable gauge liquid; bromonaphthalene dissolved the hydrogen iodide freely and very soon it decomposed, giving a dense coloration of iodine, which proceeded to attack the mercury. Oils containing unsaturated hydrocarbons are useless as they are all attacked by HI.

The difficulty was finally surmounted in the following way. A length of about 70 cm. of 1-mm. capillary tubing was inserted between B and H (fig. 2), with a vertical spiral of 5-mm. tubing on the side nearest B. Air was allowed to remain on the side of the capillary nearest the gauge, and bromonaphthalene was again used as the liquid. Then, during the course of an experiment, only the HI that diffused along the capillary could reach the gauge and most of this dissolved in some of the bromonaphthalene placed in the bulb H. It was found that the liquid in the gauge tubes remained free from contamination for hours, though the liquid in H became deeply coloured with iodine. The spiral was inserted so that any small quantity of air diffusing backwards through the capillary would have a greater distance to travel before reaching B.

With this modification of the apparatus, the viscosity experiments were carried out exactly as for the other gases, titrating with the same standard

solutions. On account of the slow decomposition of HI in sunlight, the whole experiment was performed in the dark,\* using electric light only when required to take readings. Decomposition with heat proceeds but slowly below 180° C. (Hautefeuille). In view of the above circumstances, it is probable that the results for HI are not quite so reliable as those for HCl and HBr.

The set of values of  $\eta$ , at the lower temperature recorded in Table IV, obtained with varying pressure differences, as always, is evidence that the difficulties had been practically overcome. But at the steam temperature a new difficulty presented itself. The calculated value of  $\eta$  decreased in a regular manner during the two hours over which the experiments extended, and it was noticed that at one point of the experimental capillary there was a fine yellow deposit, probably of a volatile phosphorus compound. Some iodine was also at first deposited where the tube left the steam-jacket, but after some time this disappeared. It was considered that the most satisfactory way of ascertaining the new constant of the tube was to redetermine  $\eta$  at the lower temperature without interrupting the flow of gas. This was accordingly carried out immediately after the last determination at steam temperature, and the value of  $\eta$  found was  $1.842 \times 10^{-4}$ , as compared with  $1.873 \times 10^{-4}$  previously. The difference is of the same order as the decrease in  $\eta_{100}$  during the set of readings, and indicates a gradual increase in the apparatus constant. The observed mean of  $\eta_{100}$  was therefore corrected by inserting the probable mean value of the constant at the time of the observations. Whatever the cause of the regular increase in the apparatus constant, this method of correction certainly eliminates the error more nearly than by redetermining it with air.

The density of hydrogen iodide was found experimentally by the method previously described, and, owing to the greater uncertainty in the molecular composition of this gas, especially at 100° C., the necessity for doing so is still greater. The values obtained and used in the calculation of  $\eta$  are as follows:—

At 20.6° C. and 765.1 mm.,  $v = 2353$  c.c. per litre N/10.

At 100.2° C. and 766.1 mm.,  $v = 2292$  c.c.     ,,     ,,

(The molecular weight values under these conditions are 2392 and 3037 c.c. respectively.)

\* Lemoine, 'Compt. Rend.,' vol. 85, p. 144 (1877).

Table IV.

$t$ °C.	$\eta_t \times 10^4$ .	$t$ °C.	$\eta_t \times 10^4$ .	$\eta_{100} \times 10^4$ , corrected.	Sutherland's constant C.
20·6	1·879 1·871 1·865 1·873 1·877	100·2	2·396 2·391 2·388 2·387 2·387 2·373 2·372		
Means ...	1·873 $\pm 0\cdot0016$		2·385 $\pm 0\cdot0023$	2·404 $\pm 0\cdot0023$	390

*Summary of Results.*

The results for the three gases are summarised in Table V, the values of C being used to extrapolate over the small ranges to  $\eta_0$  and  $\eta_{100}$  from the experimental data.

Table V.

	$\eta_0 \times 10^4$ .	$\eta_{100} \times 10^4$ .	C.
HCl	1·332	1·837	357
HBr	1·710	2·365	375
HI	1·731	2·403	390

In conclusion, I wish to express my gratitude to Prof. Rankine for helpful suggestions and for the kind interest he has taken in this work.

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*On the Numerical Solution of Linear Integral Equations.*

By H. BATEMAN.

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§ 1. *Introduction.*

The numerical solution of linear integral equations of the types studied by Volterra has formed the subject of a recent memoir by E. T. Whittaker.\* Numerical methods are needed also for the solution of the linear integral equation studied by Fredholm† and Hilbert‡ and the object of this paper is to describe a method which may sometimes be useful.

The linear integral equation of the second kind,

$$f(s) = \phi(s) - \lambda \int_0^1 \kappa(s, t) \phi(t) dt, \quad (1)$$

may be solved for the unknown function  $\phi(t)$  either directly or indirectly. In the direct methods of solution the function  $\phi(t)$  is expressed by means of infinite series of terms involving repeated integrals. In the so-called method of Neumann only one infinite series is used, while in the more complete method of Fredholm the function  $\phi(t)$  is expressed as the ratio of two infinite series which converge for all values of the parameter  $\lambda$ . The method of Neumann has been employed on many occasions to obtain numerical results and is generally more convenient to use than Fredholm's method on account of the great complexity of the expressions occurring in Fredholm's series. There are occasions, however, when the Neumann series fails to converge, or converges only slowly, and then some other method such as Fredholm's must be used. It seems desirable if possible to devise simple approximate methods which possess some of the advantages of Fredholm's method, because in many cases the evaluation of repeated integrals becomes very tedious and the use of the direct methods of solution becomes impracticable except for a rough approximation.

Of the indirect methods of solution, we shall be concerned here with one which depends on the use of an approximate expression for the kernel of the integral equation. E. Schmidt§ has already sketched a method in which the kernel  $\kappa(s, t)$  is replaced by an approximate expression

$$\bar{\kappa}(s, t) = \sum_{m=1}^n \alpha_m(s) \beta_m(t),$$

\* E. T. Whittaker, 'Roy. Soc. Proc.,' A, vol. 94, p. 367 (1918).

† I. Fredholm, 'Acta Math.,' vol. 27 (1903).

‡ D. Hilbert, 'Gött. Nachr.,' 1904.

§ E. Schmidt, 'Math. Ann.,' vol. 63, p. 433 (1907); vol. 64, p. 161 (1907).

consisting of a finite number,  $n$ , of products of functions of  $s$  and  $t$ . It is known that the solving function for this approximate kernel can be written down in finite terms\* and the solution of the integral equation with this approximate kernel can be regarded as an approximate solution of the original integral equation. The success of the method evidently depends upon an appropriate choice of the functions  $\alpha_m(s)$ ,  $\beta_m(t)$ . Schmidt has something to say on this matter; in particular, he indicates how the functions  $\alpha_m(s)$ ,  $\beta_m(t)$  must be chosen so as to make the double integral

$$\int_0^1 \int_0^1 [\kappa(s, t) - \pi(s, t)]^2 ds dt$$

a minimum. The required functions  $\alpha_m(s)$ ,  $\beta_m(t)$  turn out to be the first  $n$  pairs of normal orthogonal functions associated with the kernel  $\kappa(s, t)$  in a manner described by Schmidt. These functions are generally difficult to find, consequently this best method of approximating to the kernel is generally useless for an easy numerical solution of the integral equation.

In the following paper we shall show that by making a different choice of the functions  $\alpha_m(s)$ ,  $\beta_m(t)$  we can obtain formulæ which are quite suitable for numerical work.

## § 2. *Method of Approximation.*

We shall use the term solving function to denote a function  $K(s, t)$  such that the solution of the integral equation (1) may be expressed in the form

$$\phi(s) = f(s) + \lambda \int_0^1 K(s, t) f(t) dt \quad (2)$$

when  $f(s)$  is any continuous function. Our method is now based on the following general theorem.†

Let  $\kappa(s, t)$  be a kernel for which the solving function  $K(s, t)$  is known, then if  $f_1(s)$ ,  $f_2(s) \dots f_n(s)$ ;  $g_1(t)$ ,  $g_2(t) \dots g_n(t)$  are given continuous functions and  $a_{lm}$  ( $l, m = 1, 2, \dots n$ ) given constants, the solving function  $H(s, t)$  for a kernel  $h(s, t)$ , defined by the equation

$$\left| \begin{array}{cccc} \kappa(s, t) - h(s, t) & f_1(s) & f_2(s) & \dots & f_n(s) \\ g_1(t) & a_{11} & a_{12} & \dots & a_{1n} \\ g_2(t) & a_{21} & a_{22} & \dots & a_{2n} \\ \dots & \dots & \dots & \dots & \dots \\ g_n(t) & a_{n1} & a_{n2} & \dots & a_{nn} \end{array} \right| = 0, \quad (3)$$

\* E. Goursat, 'Bull. Soc. Math. France,' vol. 35, p. 163 (1907); H. Lebesgue, *ibid.*, vol. 36, p. 3 (1908); E. Schmidt, *loc. cit.*

† 'Mess. of Math.,' April (1908).

is given by the equation

$$\begin{vmatrix} K(s, t) - H(s, t) & \phi_1(s) & \phi_2(s) & \dots & \phi_n(s) \\ \chi_1(t) & A_{11} & A_{12} & \dots & A_{1n} \\ \chi_2(t) & A_{21} & A_{22} & \dots & A_{2n} \\ \dots & \dots & \dots & \dots & \dots \\ \chi_n(t) & A_{n1} & A_{n2} & \dots & A_{nn} \end{vmatrix} = 0, \quad (4)$$

where

$$\left. \begin{aligned} \phi_l(s) &= f_l(s) + \lambda \int_0^1 K(s, t) f_l(t) dt, \\ \chi_m(t) &= g_m(t) + \lambda \int_0^1 g_m(s) K(s, t) ds, \\ A_{lm} &= a_{lm} + \lambda \int_0^1 g_l(x) \phi_m(x) dx \end{aligned} \right\}. \quad (5)$$

The functions occurring in this theorem are all supposed to be completely defined in the intervals  $(0 \leq s \leq 1)$ ,  $(0 \leq t \leq 1)$  and to be continuous throughout these intervals.

We are interested chiefly in the case when  $\kappa(s, t) = 0$ ,  $K(s, t) = 0$ , then  $\phi_l(s) = f_l(s)$ ,  $\chi_m(t) = g_m(t)$ , and the value of  $A_{lm}$  is at once known.

Let us suppose that  $w(s, t)$  is the kernel of an integral equation

$$\alpha(s) = \beta(s) - \lambda \int_0^1 w(s, t) \beta(t) dt \quad (6)$$

whose approximate solution is desired.

Putting

$$f_m(s) = -w(s, t_m), \quad g_l(t) = -w(s_l, t), \quad a_{lm} = -w(s_l, t_m), \quad (7)$$

where  $s_1, s_2, \dots, s_n$ ;  $t_1, t_2, t_n$  are particular values of  $s$  and  $t$  belonging to the interval  $(0, 1)$  it is clear that equation (3) becomes

$$\begin{vmatrix} h(s, t) & w(s, t_1) & w(s, t_2) & \dots & w(s, t_n) \\ w(s_1, t) & w(s_1, t_1) & w(s_1, t_2) & \dots & w(s_1, t_n) \\ w(s_2, t) & w(s_2, t_1) & w(s_2, t_2) & \dots & w(s_2, t_n) \\ \dots & \dots & \dots & \dots & \dots \\ w(s_n, t) & w(s_n, t_1) & w(s_n, t_2) & \dots & w(s_n, t_n) \end{vmatrix} = 0. \quad (8)$$

This equation defines a function  $h(s, t)$ , which satisfies the conditions

$$\left. \begin{aligned} h(s, t_m) &= w(s, t_m) & (0 \leq s \leq 1) & \quad (m = 1, 2 \dots n) \\ h(s_l, t) &= w(s_l, t) & (0 \leq t \leq 1) & \quad (l = 1, 2 \dots n) \end{aligned} \right\}. \quad (9)$$

The function  $h(s, t)$  thus agrees in value with the function  $w(s, t)$  over a network of lines in the  $(s, t)$  plane; it thus represents a good approximation

to the function  $w(s, t)$ . It follows, moreover, from formula (4) that the solving function  $H(s, t)$  can be written down, and so an approximate solution of the integral equation (6) is furnished by the formula

$$\beta(s) = \alpha(s) + \lambda \int_0^1 H(s, t) \alpha(t) dt. \quad (10)$$

It should be noticed that the above approximate representation of  $w(s, t)$  becomes exact when  $w(s, t)$  is of the form

$$w(s, t) = \sum_{m=1}^n p_m(s) q_m(t),$$

it fails when  $w(s, t)$  is the sum of less than  $n$  products of type  $p(s)q(t)$ , for then the co-factor of  $h(s, t)$  in the determinant (3) vanishes. Approximate values of the singular values of  $\lambda$  for the integral equation may be obtained by equating to zero the coefficient of  $H(s, t)$  in equation (4). It should be remarked that, when  $n$  is even, the approximate values of  $\lambda$  thus obtained may be complex even when the exact values of  $\lambda$  are all real.

### § 3. *Illustrative Example.*

Let us apply our method to Hilbert's integral equation, in which the kernel  $w(s, t)$  is defined by the equations

$$w(s, t) = \begin{cases} s(1-t) & s \leq t \\ t(1-s) & s \geq t \end{cases}$$

We have

$$A_{lm} = -w(s_l, t_m) + \lambda \int_0^1 w(s_l, x) w(x, t_m) dx.$$

$$\text{Now} \quad \int_0^1 w(s, x) w(x, t) dx = \begin{cases} \frac{1}{6} s(1-t)(2t-s^2-t^2) & s \leq t, \\ \frac{1}{6} t(1-s)(2s-s^2-t^2) & s \geq t, \end{cases}$$

hence the value of  $A_{lm}$  is easily found.

We shall interest ourselves simply in the way in which our method enables us to approximate to the singular values of  $\lambda$ , for which the homogeneous equation

$$\phi(s) = \lambda \int_0^1 w(s, t) \phi(t) dt$$

can be satisfied. It is known that the exact singular values of  $\lambda$  are  $\pi^2, (2\pi)^2, (3\pi^2), \dots$ , while, according to our method of approximation, they should be given approximately by the determinant  $|A_{lm}| = 0$ , the degree of approximation being better the larger the value of  $n$ . Let us take  $n = 5$ ,

$$s_1 = t_1 = \frac{1}{6}, \quad s_2 = t_2 = \frac{2}{6}, \quad s_3 = t_3 = \frac{3}{6}, \quad s_4 = t_4 = \frac{4}{6}, \quad s_5 = t_5 = \frac{5}{6},$$

then if  $\lambda = 216x$  the equation for  $\lambda$  may be written in the form

$$\begin{vmatrix} 5(1-10x) & 4(1-19x) & 3(1-26x) & 2(1-31x) & 1-34x \\ 4(1-19x) & 8(1-16x) & 6(1-23x) & 4(1-28x) & 2(1-31x) \\ 3(1-26x) & 6(1-23x) & 9(1-18x) & 6(1-23x) & 3(1-26x) \\ 2(1-31x) & 4(1-28x) & 6(1-23x) & 8(1-16x) & 4(1-19x) \\ 1-34x & 2(1-31x) & 3(1-26x) & 4(1-19x) & 5(1-10x) \end{vmatrix} = 0.$$

The determinant is easily evaluated by repeatedly subtracting rows and columns and we obtain the equation

$$130x^5 - 441x^4 + 488x^3 - 206x^2 + 30x - 1 = 0,$$

$$\text{i.e.,} \quad (x-1)(2x-1)(5x-1)(13x^2-22x+1) = 0.$$

Approximate singular values of  $\lambda$  are thus

$$\lambda_1 = 10.09, \quad \lambda_2 = 43.2, \quad \lambda_3 = 108, \quad \lambda_4 = 216, \quad \lambda_5 = 355.2.$$

The first is equal to  $\pi^2$  within about 2 per cent., the second differs from  $4\pi^2$  by about 9 per cent. while the errors in the other cases are larger still. If with  $n = 3$  we take

$$s_1 = t_1 = \frac{1}{4}, \quad s_2 = t_2 = \frac{1}{2}, \quad s_3 = t_3 = \frac{3}{4},$$

we shall find the approximate values

$$\lambda_1 = 10.37, \quad \lambda_2 = 48.13, \quad \lambda_3 = 126.13.$$

With  $n = 1$  and  $s_1 = t_1 = \frac{1}{2}$  we find simply the approximate value

$$\lambda_1 = 12.$$

In the case when  $n = 5$ , the percentage error in the value of  $\lambda$  is roughly proportional to  $\lambda$ . When we are dealing with the solution of the equation (6) instead of the homogeneous equation, we can generally expect the percentage error to increase with  $\lambda$ . If we wish our answer to be correct within 1 per cent. when the value of  $\lambda$  is in the neighbourhood of the first singular value, we should take  $n = 7$  at least, with a value of  $\lambda$  equal to about half the first singular value, it may be sufficient to take  $n = 5$ , for values of  $\lambda$  larger than the first singular value, still higher values of  $n$ , such as 9 or 11, may be needed to give the desired degree of approximation.

#### § 4. *Polynomial Kernel.*

The method of § 2 can be extended without difficulty to the case of a system of integral equations by making use of Fredholm's well known device. It may also be extended in other directions; we may, for instance, write

$$f_m(s) = \kappa(s, t_m) - w(s, t_m), \quad g_l(t) = \kappa(s_l, t) - w(s_l, t),$$

$$a_{lm} = \kappa(s_l, t_m) - w(s_l, t_m),$$



where  $\kappa(s, t)$  is a kernel for which the solving function  $K(s, t)$  is known. The function  $h(s, t)$  is then equal to  $w(s, t) - k(s, t)$  over the lines of a network.

Another method depends on the use of an approximate polynomial representation of the kernel  $w(s, t)$ . Let us now put

$$\kappa(s, t) = 0, \quad f_m(s) = s^m, \quad g_m(t) = t^m, \quad K(s, t) = 0,$$

then 
$$A_{lm} = a_{lm} + \lambda \int_0^1 x^{l+m} dx = a_{lm} + \frac{\lambda}{l+m+1}$$

If now the expression for  $h(s, t)$  is

$$h(s, t) = - \sum_{r=0}^n \sum_{m=0}^n b_{mr} s^r t^m,$$

where 
$$b_{mr} = 0, \quad m+r > n,$$

we may determine the constants  $a_{lm}$  by solving the equations

$$\begin{aligned} x_1 &= b_{11}y_1 + b_{21}y_2 + \dots b_{n1}y_n, \\ x_2 &= b_{12}y_1 + b_{22}y_2 + \dots b_{n-1,2}y_{n-1}, \\ &\dots\dots\dots \\ x_n &= b_{1n}y_1, \end{aligned}$$

the solutions being

$$\begin{aligned} \Delta y_1 &= a_{1n}x_n + a_{1, n-1}x_{n-1} + \dots a_{11}x_1, \\ \Delta y_2 &= a_{2n}x_n + a_{2, n-2}x_{n-1} + \dots a_{21}x_1, \\ &\dots\dots\dots \\ \Delta &= \begin{vmatrix} b_{11} & b_{21} & \dots & b_{n1} \\ b_{12} & \dots\dots\dots \\ \dots\dots\dots \\ \dots\dots\dots \end{vmatrix} \end{aligned}$$

It is clear from these equations that  $a_{mr} = 0, m+r < n+1$ , also

$$a_{1n} = \frac{\Delta}{b_{1n}}, \quad a_{2, n-1} = \frac{\Delta}{b_{2, n-1}}, \quad a_{2, n} = -\frac{\Delta b_{1, n-1}}{b_{1n}b_{2, n-1}}.$$

Our object now is to obtain an approximate representation of a kernel  $\kappa(s, t)$  by means of a polynomial in  $s$  and  $t$ , or by some other double series of functions of  $s$  and  $t$ .

Some interpolation formulæ for functions of two variables have been studied by S. Namuri.\* If we write

$$\begin{aligned} \Delta_x^l f(x+h, y) - \Delta_x^l f(x, y) &= \Delta_x^{l+1} f(x, y), \\ \Delta_y^m \Delta_x^l f(x, y+k) - \Delta_y^m \Delta_x^l f(x, y) &= \Delta_y^{m+1} \Delta_x^l f(x, y), \end{aligned}$$

\* S. Namuri, 'The Tôhoku Mathematical Journal,' vol. 18, p. 309 (1920).

for all values of  $1, m, 0, i, 2, \dots$ , it is easy to see that the operators  $\Delta_x$  and  $\Delta_y$  are permutable, in other words we have the relation

$$\Delta_y^m \Delta_x^i f(x, y) = \Delta_x^i \Delta_y^m f(x, y)$$

for all values of  $y$ . Introducing the notation

$$\binom{s}{k} = \frac{s(s-1) \dots (s-k+1)}{1 \cdot 2 \dots k},$$

the desired interpolation formula may be written

$$f(a+sh, b+tk) = \sum_{l=0}^{\mu-1} \sum_{m=0}^{\nu-1} \binom{s}{l} \binom{t}{m} \Delta_x^l \Delta_y^m f(a, b) + R_{\mu\nu},$$

$$x = a+sh, \quad y = b+tk,$$

where the remainder  $R_{\mu\nu}$  has the form

$$\binom{s}{\mu} h^\mu \frac{\partial^\mu}{\partial \alpha^\mu} f(\alpha, y) + \binom{t}{\nu} k^\nu \frac{\partial^\nu}{\partial \beta^\nu} f(x, \beta) - \binom{s}{\mu} \binom{t}{\nu} h^\mu k^\nu \frac{\partial^{\mu+\nu}}{\partial \alpha^\mu \partial \beta^\nu} f(\alpha, \beta),$$

where  $\alpha$  lies between the least and greatest of the quantities

$$a, a+h, a+2h \dots, \quad a+(\mu-1)h, a,$$

and  $\beta$  lies between the least and greatest of the quantities

$$b, b+k, b+2k \dots, \quad b+(\nu-1)k, b, y.$$

If the function  $f(x, y)$  is actually a polynomial of degree  $\mu-1$  in  $x$  and of degree  $\nu-1$  in  $y$ , the remainder vanishes.

The above method of interpolation is suitable for the case in which the function  $f(x, y)$  is known at the points of intersection of two sets of lines parallel to the axes of co-ordinates. Mamuri has extended the formula for the case in which the interval between two successive lines is not constant, but it is desirable to have a formula which is applicable when the points at which  $f(x, y)$  is known are distributed at random.

Let us consider the simple case in which there are six points,  $P_1, P_2, P_3, P_4, P_5, P_6$ , and let  $C_r = 0$  be the equation of the conic through all the points except  $P_r$ , also let  $c_r$  be the value of  $C_r$  when the co-ordinates of  $P_r$  are substituted in  $C_r$ , then if  $p_r$  denotes the value of  $f(x, y)$  at the point  $P_r$ , the required formula is

$$f(x, y) \sim \sum_{r=1}^6 p_r \frac{C_r}{c_r}.$$

When the six points are the six intersections of four lines  $L_1 = 0, L_2 = 0, L_3 = 0, L_4 = 0$ , we may write

$$C_1 = L_2 L_3, \quad C_2 = L_3 L_1, \quad C_3 = L_1 L_2, \quad C_4 = L_1 L_4, \quad C_5 = L_2 L_4, \quad C_6 = L_3 L_4.$$

These two methods, which are well known, may be extended, for when there are  $\frac{1}{2}n(n+1)$  points at which the value of  $f(x, y)$  is known, we may use

a curve of the  $(n-1)$ th degree instead of a conic, and when the  $\frac{1}{2}n(n+1)$  points lie at the intersection of  $n+1$  lines we may represent each of these curves as the product of  $(n-1)$  lines.

### § 5. Possible Applications.

It is known that many problems in the theory of elasticity may be reduced to an integral equation of the second kind or to a system of integral equations of the second kind.\* In particular, Fredholm has indicated a method of reducing a two-dimensional elastic problem to a pair of integral equations with kernels that do not become infinite within the range of integration. The torsional problem in the theory of elasticity† and many electrical problems are equivalent to well known potential problems that are reducible to integral equations of the second kind. Certain problems relating to the flexure of beams are likewise reducible to integral equations.

It is thought that the method of § 2 may be sometimes useful in dealing with such problems. It is true that the work will be laborious, but this seems unavoidable when a numerical solution is desired.

Problems relating to the critical strength of struts and structures, the vibrations of rods and membranes, the whirling of shafts, etc., may also be treated by this method, the differential equations being replaced by integral equations. It is thought, however, that in these cases the methods of approximation proposed recently by other writers‡ may be more convenient to use.

In the case of the equation of a vibrating membrane

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + k^2 V = 0,$$

we may employ Whittaker's solution§

$$V = \int_0^{2\pi} e^{ik(x \cos \alpha + y \sin \alpha)} \phi(\alpha) d\alpha.$$

\* See, for instance, E. and F. Cosserat, 'Comptes Rendus,' Paris, vol. 133 (1901); I. Fredholm, 'Arkiv för Math. och Fys.,' vol. 2 (1906); G. Lauricella, 'Atti Lincei' (5), vol. 15, pp. 426, 610, vol. 15, pp. 75-83 (1906); 'Il Nuovo Cimento' (5), vol. 13 (1907), four papers; 'Rend. Lincei' (1907); 'Acta Math.' (1908-9); T. Boggio, 'Atti Lincei,' vol. 16, pp. 248, 441 (1907); Marcolongo, 'Toulouse Ann.' (1908); J. Hadamard, 'Mémoires de l'Institut' (1908); A. Korn, 'Ann. École Normale' (3), vol. 25 (1908); Zaremba, *ibid.*, p. 337; A. Haar, 'Gött. Nach.' (1907); O. Tedone, 'Rend. Lincei,' p. 232 (1904); C. E. Weatherburn, 'Phil. Mag.,' vol. 32, p. 15 (1916); 'Mess. of Math.,' vol. 47, p. 114 (1917).

† Cf. L. Bairstow, 'Roy. Soc. Proc.,' A, vol. 95, p. 457 (1919).

‡ W. L. Cowley and H. Levy, 'Roy. Soc. Proc.,' A, vol. 95, p. 440 (1919); 'Phil. Mag.,' vol. 41, p. 584 (1921); A. A. Griffith, 'National Advisory Committee for Aeronautics,' R. and M. 545 (1918-19); R. V. Southwell, 'Phil. Mag.,' vol. 41, p. 419 (1921).

§ 'Math. Ann.' (1903); Whittaker-Watson, "Modern Analysis."

If the boundary condition is

$$V = 0 \text{ when } x = r(\theta) \cos \theta, \quad y = r(\theta) \sin \theta,$$

we obtain the integral equation

$$0 = \int_0^{2\pi} e^{ikr(\theta) \cos(\theta - \alpha)} \phi(\alpha) d\alpha,$$

which may be regarded as a limiting case of the homogeneous equation

$$\mu(k) \phi(\theta) = \int_0^{2\pi} e^{ikr(\theta) \cos(\theta - \alpha)} \phi(\alpha) d\alpha.$$

We may apply our method of approximation to obtain the possible values of the functions  $\mu(k)$ . Equating these to zero we obtain the possible values of  $k$ .

*The Atomic Process in Ferromagnetic Induction.*

By Sir J. ALFRED EWING, K.C.B., F.R.S.

(Received November 29, 1921.)

The object of this paper is to amend, in an important particular, the theory of ferromagnetic induction put forward by me more than 30 years ago,\* and to describe a new model. That theory was itself a modification of the earlier theory of Weber. To Weber is due the fundamental notion that a substance contains minute particles, each of which acts as a magnet, and that in the process of magnetising a ferromagnetic substance these are turned into more or less complete alignment. The ultimate magnetic particles used to be called "molecular magnets": we now recognise them as attributes of the atom, not of the molecule, and (in all probability) they derive their magnetic moment from the circulation of electricity in electron orbits or in ring electrons. What turns is not the molecule nor the atom, but something within the atom.

The characteristics which distinguish ferromagnetic substances from other paramagnetics are: (1) the much larger amount of magnetism they can acquire under the action of an impressed field; (2) the fact that the acquired magnetism tends towards a saturation limit when the field is progressively increased; (3) the fact that the acquired magnetism shows hysteresis with

\* "Contributions to the Molecular Theory of Induced Magnetism," 'Roy. Soc. Proc.' vol. 48, p. 342 (1890); 'Phil. Mag.,' September, 1890. See also 'Magnetic Induction in Iron and other Metals,' Chap. XI.

respect to variations of the field, except in certain small initial changes. Weber's theory explained (1) and (2). My modification of it explained, in addition, (3) as an effect of the irreversible action which occurs when the equilibrium of a magnetic element becomes unstable through change in the externally impressed magnetic force, and it swings over, with dissipation of energy, into a new position of stability. The stability in both positions is sufficiently explained by magnetic forces only. In breaking away from one stable position it is deflected at first in a quasi-elastic (reversible) manner until the external force reaches a certain value at which the equilibrium is upset. The essence of hysteresis is the turning from one position of stability to another, through a region of instability. If the conditions are such that there is no unstable phase in the turning, then there is no dissipation of energy, and consequently no hysteresis. This occurs in very feeble magnetisation, when the deflections are reversible; it also occurs if the piece be caused to rotate in a field of great strength. J. Swinburne pointed out that, as a consequence of my theory, hysteresis should vanish when a cylinder of ferromagnetic metal is rotated in a very strong field,\* and this curious result was confirmed experimentally by F. G. Baily.†

So far the theory is, I think, still valid. What needs amendment is that the magnetic control of each Weber element was ascribed simply to the action of its neighbours, namely, other Weber elements which were also liable to be turned by a sufficient impressed force. The Weber elements were treated as deriving their stability by forming rows or pairs, in which the mutual magnetic actions between similar neighbouring elements in the row constituted the controlling force. Hysteresis was found when rows (or pairs) broke up and new rows (or pairs) were formed. A model was constructed to illustrate this action, with groups of pivoted permanent magnets, and it was shown to reproduce with remarkable completeness, in a qualitative manner, the chief features of magnetisation as observed in iron and other ferromagnetic substances.

One of these features is that there is no more than a very small reversible change of magnetism, before hysteresis asserts itself, when a field begins to be applied, or begins to be removed, or to be re-applied. Thus in the magnetisation of common soft iron from a neutral state the initial stage, which was shown by the late Lord Rayleigh‡ to be reversible, passes into an irreversible stage, involving hysteresis, when only a very small fraction

\* 'Industries,' September 19, 1890.

† 'Phil. Trans.,' A, vol. 187, p. 715 (1896).

‡ 'Phil. Mag.,' March, 1887.

of the magnetism of saturation has been acquired, say about 10 or 15 units out of 1700. This implies that the average amount of reversible deflection on the part of the Weber element before it becomes unstable is less than  $1^\circ$ . In order to reproduce this feature in a model with pivoted magnets, we have to space the magnets so closely that when they group themselves in rows the poles are very near together. From calculations relating to the stability of a row of pivoted magnets, which I have checked experimentally by observing the behaviour of pairs and rows of ball-ended magnets in the field of a pair of coils arranged as in the Helmholtz galvanometer, I find that if the limiting stable deflection is to be of the order of  $1^\circ$ , the ratio  $a/r$ , where  $a$  is the half distance between centres and  $r$  is the half length of each magnet, must not exceed about 1.025.

On the assumption that each atom in a crystal of iron contains one Weber element, it is easy to calculate what would be the strength of the field which would rupture a row, with given orientation, if the poles of the elements are spaced as closely as this condition demands. When the calculation is made it gives a field that is immensely greater than the field actually required, in iron, to pass from the reversible to the irreversible stage. The calculated field, for such rows (assuming the usual laws of force to apply) is some thousands of times greater than that at which hysteresis begins to show itself.\* I have therefore been obliged to abandon the idea of representing the process of magnetisation of iron, even roughly, by means of magnetic elements all free to turn and controlling one another from atom to atom in the crystal. But another type of model has now suggested itself which seems to offer a satisfactory solution.

Imagine a pivoted magnet W (fig. 1), acted upon by a deflecting field H, and controlled by two fixed magnets A and B, which point in opposite directions, so that the control depends on the difference of their effects. Imagine a slight lack of symmetry, a difference either in strength or in nearness, so that the fixed magnet A acts rather more strongly than the fixed magnet B. Then W is in a feebly stable condition, which a weak

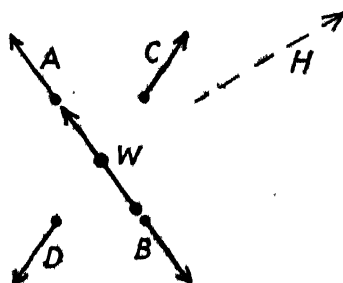


Fig. 1.

\* In fairly pure soft iron the field that is sufficient to reach the limit of elastic magnetisation is about 1 C.G.S. unit, and in the purer iron that is obtained by electrolytic deposition, with subsequent melting *in vacuo*, it may be only about 0.1 C.G.S. unit. (See the experiments of Yensen, 'Illinois University Bulletins,' Nos. 72, 83, 95.)

deflecting field will suffice to disturb; and *provided the poles of A and B are near those of W*, there will be no more than a small reversible deflection before the equilibrium is upset. This group accordingly satisfies the two necessary conditions which were incompatible in a pair or row of pivoted magnets; it combines small limiting stable deflection with easy rupture of stability. Assume now that lying along a transverse line more nearly in the direction of H, there are two other fixed magnets C and D, also slightly unequal in their effects. When W breaks away from A and B it may swing (with dissipation of energy) into a stable relation with C and D, until finally when H is sufficiently increased it will be pulled out of that into nearly perfect parallelism with H. It will be obvious that such a model—when imagined as extended into three dimensions—reproduces ferromagnetic phenomena. In applying magnetising force to a piece of metal made up of groups of such atoms we should clearly find a slow beginning, a subsequent rapid rise, and a final slow approach to saturation; and in removing the force we should find residual magnetism.

I have made a one-plane model with ball-ended magnets, each consisting of a strongly magnetised straight steel wire with its ends screwed into quarter-inch steel balls. The central magnet W is pivoted like a compass needle. Each of the controlling magnets, A, B, C, D, is held in a fixed support, but so that it can be moved towards or away from the pivoted magnet, thus allowing the control to be made as weak or as strong as may be desired. When the group is set in a field which is increased, reduced, reversed and so on, or when the group is caused to turn in a constant field, the features observed in cyclic and other processes of magnetisation are very exactly imitated. The model may be made more realistic by including a number of similar contiguous groups, but a single group suffices to illustrate the action.

It remains to be seen how the parts which make up the model can be thought of as having equivalents in the structure of the atom. One has to imagine the electrons of each atom as furnishing two types of magnetic element, a turning element within the atom, and other elements at a greater distance from the centre, which are held fixed (more or less completely) as a consequence of the relation between the atom and the neighbouring atoms of the crystal. Take, for instance, a structure such as A. W. Hull has suggested, on the basis of his X-ray analysis, as a probable structure for the iron atom,\* in which two of the electrons, on opposite sides of the nucleus, form a doublet, and the remaining twenty-four are grouped in octets, further from the nucleus, along the diagonals of a cube. Think provisionally of these

\* "The Crystal Structure of Iron," 'Phys. Rev.,' vol. 9, p. 85 (1917).

octets as making up fixed magnetic elements which correspond to A, B, C, and D, of the model, with axes that lie in the cube diagonals of the atom, coinciding (it may be supposed) with the trigonal axes of the crystal. They point radially inwards, and all their inner "poles" are of the same name. In the inner space the doublet, which corresponds to W, the Weber element of the model, turns under the influence of any impressed field. When there is no external field, the Weber element may be in any one of eight positions of stability, pointing towards one of the fixed elements, namely towards one of the eight corners of a cube.\* Its irreversible passage from one position of stability to another is what constitutes hysteresis. Its small reversible deflection, before breaking away from any one position of stability, constitutes the initial quasi-elastic stage of magnetisation. The range of this deflection is small because the controlling poles are near it. The stability is feeble because the control is differential: it depends on the nearly balanced action of large opposing forces which are separately applied by two fixed elements.

We have to postulate a small defect of symmetry in their action, in order that the Weber element may be stable. In any position which it may assume, the circumferential magnetic elements must act on its two ends somewhat unequally. The attraction in the model between one end and the unlike pole near it must be slightly stronger than the repulsion between the other end and the like pole near that. More than one cause may be operative in producing a corresponding asymmetry in the atom. The circumferential magnetic elements may not be strictly fixed, relative to the centre of rotation of the Weber element, but may be capable of small displacements of a kind to cause the unlike pole of one to act more strongly and the like pole of the other to act less strongly, or the Weber element may admit of being pulled a little nearer the attracting pole. It is at least possible that such displacements may result from the mutual magnetic forces between the Weber element and the fixed elements. The model with ball-ended steel magnets behaves, in fact, in a way that illustrates just such an

\* According to Hull's X-ray analysis, the space-lattice of an iron crystal is the centred cube: the spacing of the atoms is closest along each trigonal axis. In the model, as shown in the figure, the plane of the sketch is that of two trigonal axes. Hull finds that the side of the unit cube—namely, the distance between atom centres along the cubic axes of the crystal—measures  $2.86 \times 10^{-8}$  cm. Since the space-lattice is the centred cube, there are two atoms in each unit cube, and  $\frac{2}{(2.86 \times 10^{-8})^3}$  atoms in a cubic centimetre. We may take the magnetism of saturation of iron to be 1700 C.G.S. units. Hence, assuming that there is one rotatable Weber element in each atom its moment is  $\frac{1700 (2.86 \times 10^{-8})^3}{2}$  or  $2 \times 10^{-20}$  very nearly.



action, for the magnetic rigidity of the bars is imperfect, and when the distances between the balls are adjusted to be equal at both ends the pivoted magnet is found to be stable, because magnetic induction has slightly altered the distribution of magnetism of the bars, bringing unlike poles nearer together, and setting like poles further apart.

Further, some small geometrical asymmetry may be set up by the action of neighbouring atoms. Effects of strain on magnetic quality—which are known to be large and complex—may be explainable by reference to displacements of the external electrons and consequent disturbances of the balance on which the control of the Weber element depends. Even in unstrained iron an impurity may, in general, be expected to restrain the response to an impressed field by disturbing this balance. When an atom of foreign matter finds a place in the space-lattice the symmetry of the neighbours must be affected by its presence, the grouping of their electrons will be more or less distorted and the Weber elements in them may consequently be unduly stabilised. This is borne out by the observed fact that the hysteresis of iron becomes in general less and less, and the susceptibility becomes greater, the more completely all impurities, including dissolved gases, are eliminated. Again, in a chemical compound of iron the iron atom is unsymmetrically surrounded and its magnetic properties become widely different from those of an atom of uncombined iron. In these respects, and in others such as the effects of vibration and temperature, this new model seems to give results that agree with observation.

Objection may be taken that the Weber element of the model is too much buried within the shells of outer electrons to be susceptible to the influence of stress and vibration, or to the presence of another chemical constituent in the crystal. But it should be noted that according to the view I have endeavoured to set out, its stability depends on a delicate balance between forces which are exerted on it by the outer electrons, and will be readily affected by anything that affects them. That only an inner and probably small constituent of the atom should be liable to turn, in the process of magnetisation, agrees with the observations of A. H. Compton and O. Rognley, who could detect no change in the X-ray spectrum reflected from the face of an iron crystal when the crystal was magnetised.\*

Their conclusion that the atom itself does not turn may be deduced without X-ray analysis from the simple consideration that, if the atom turned, we should expect the cohesion and rigidity of the piece to be much affected

\* 'Phys. Rev.,' vol. 16, p. 464 (1920). From earlier experiments on the dispersion of X-rays, K. T. Compton and Trousdale had inferred that the Weber element is not a molecule or group of atoms.—'Phys. Rev.,' vol. 5, p. 315 (1915).

during a process such as the reversal of a strong external field, and of that there is no evidence. Everything points to the idea that in each atom of the crystal a shell of outer electrons is locked in relation to its neighbours, except for small relative movements such as occur through thermal agitation or mechanical straining, and that the Weber elementary magnet is constituted by other electrons nearer the nucleus.

We are not here concerned with the nature of the forces between neighbouring atoms in the space-lattice. If they are largely electromagnetic the contiguous electron orbits in any two nearest neighbours may be oppositely directed. In a model of iron, for instance, we might imagine one atom to have the equivalent of eight north poles on its surface, while each of its eight nearest neighbours has eight south poles on its surface. The space-lattice being the centred cube, each atom, under these conditions, would be surrounded by eight nearest neighbours of opposite polarity to itself. Such a grouping would obviously lend itself well to the building up of a model crystal in which the magnetic property of the electrons was represented by little bar magnets, facing radially, but in opposite senses in the shells of any two neighbouring atoms. So far as the action of the inner element is concerned—the element which turns in response to an applied field—it is indifferent in which sense the controlling magnets face, provided they all face in the same sense in any one atom.

A model satisfying the essential conditions may take more than one form. The form that has been described is appropriate if the electrons have orbits whose dimensions are small relatively to the size of the atom, or are themselves small rings. The conditions are simply that one or more of the orbits or rings, with an unbalanced magnetic moment, should be capable of orientation under control exerted by other parts of the atom (which are held relatively fixed), and that it should be deflected through only a small angle before becoming unstable, when it turns into another position of stability; and further that the stability in each position should be weak. The combination of weak stability with a narrow range of stable deflection is secured by the differential character of the control: it depends on there being a slight inequality between two strong but oppositely directed forces. These features are exemplified in the model already described (fig. 1). Another model, which also exemplifies them, but in a manner more suggestive of large orbits, is illustrated in fig. 2. There *W* (which represents the Weber element) is a coil carrying a current and free to turn about an axis *ab*. *A*' and *B* are fixed controlling coils in close proximity, with currents as shown by the arrows, arranged to exert slightly unequal forces on *W*. By adjusting the distances, or the strength of the currents, the resulting control can be made as small as

is desired. In the model there are two more controlling coils set in a plane transverse to that of the first pair, so that *W* may turn from one stable position to another (see plan, fig. 2*a*). In turning under the influence of an impressed field, it is deflected stably through a narrow range before becoming unstable.

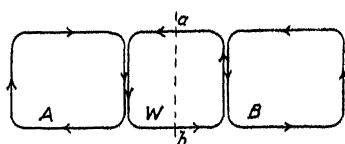
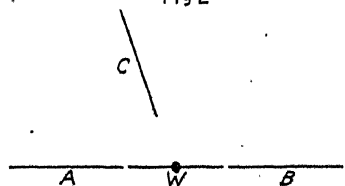


Fig 2

Fig 2*a*

It will be noted that in this model the Weber element is constituted by a single electron orbit, instead of being a doublet as in fig. 1. But the conditions governing the stability are in essential points the same; it still depends on the difference between two nearly equal forces, and this allows the control to be weak although the range of stability is kept small.

An interesting variant of this model, and one that perhaps comes nearer the real structure of the atom, is obtained by making the fixed coils *A* and *B* overlap sufficiently to embrace *W*, as in fig. 3. There *A* and *B* represent coplanar elliptic orbits with a common focus which is also the centre of a circular orbit, *W*, representing the Weber element. In the model the fixed controlling coils *A* and *B* are elliptical in form and are set as nearly as may be in one plane. *W* is a circular coil pivoted about the axis, *ab*. As before, the model is to be understood as having a second pair of

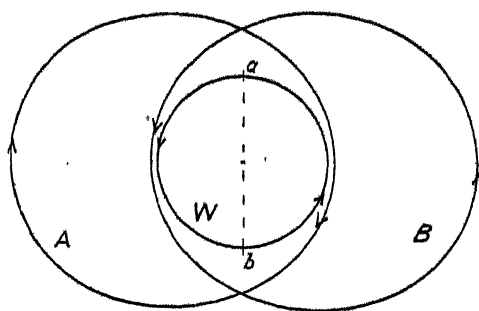


Fig 3.

similar controlling coils set in a transverse plane; and it is easy (in imagination) to extend the construction to three dimensions, adding other controlling coils and allowing *W* freedom to turn about any axis in its own plane. This gives a model embodying the same principles, with all its coils in the form of orbits which have the nucleus of the atom at their focus.

With regard to the inequality of forces on which the control depends, there is an important distinction between (1) any inequality that may arise from the mutual action between the Weber element itself and the fixed elements; and (2) any inequality that may arise from strain in the piece as a whole, or from the influence of unsymmetrically placed neighbouring atoms. In case (1) the inequality is transferred from one to another pair of controlling elements as the Weber element turns from one position of stable equilibrium to another. Thus in the model (fig. 1), when *W* points towards *A* and *B*, there is inequality in the action of *A* and *B*, *A* being, by hypothesis, caused to act more strongly as an effect of the proximity to it of the unlike pole of *W*; but when *W* turns into another stable position between *C* and *D*, *C* for the same reason acts on it more strongly than *D*, and so on with any other pair. Except for the distorting influence of *W*, the atom may be isotropic in respect of the grouping of the elements *A*, *B*, *C*, *D*, etc., and the magnetic qualities of the piece will then be the same along these various axes. In case (2) on the other hand, there is an asymmetry which persists in particular directions within the atom while *W* turns, and its influence on the control is superposed on any that *W* itself produces, with the result that the piece may exhibit differences of susceptibility and retentiveness in different directions.

It is well known that a homogeneous ferromagnetic metal becomes magnetically anisotropic under strain; it is also well known that a compound crystal, such as pyrrhotite, has widely different magnetic qualities in different directions. I suggest that these are examples of case (2); they are effects which can be imitated in the model by setting up differences in the closeness of the paired controlling magnets or coils along different axes, and by making the turning element contain a sufficient number of magnet poles or coils.

It may be convenient to recapitulate the chief points of this paper. While retaining the idea of magnetic control of the Weber element as determining the susceptibility and hysteresis of ferromagnetic substances, I have been led to replace my older model by a new one in which the Weber element in each atom is controlled by other parts of the same atom instead of only by the Weber elements in the adjoining atoms. The position of the atom in the crystal secures that these parts are more or less completely fixed. They probably constitute a shell, or series of concentric shells, within which the Weber element may turn in response to an impressed field, and by which its turning is so controlled that it is capable of small stable deflections and of large irreversible deflections, so that it may swing over with dissipation.

of energy from one stable position to another when the range of stable deflection is exceeded. This range is in general very narrow. Experiments on the magnetic quality of soft iron show that it is less, in that metal, than  $1^\circ$ . At the same time they show that the control must be weak, for a small magnetising force suffices to upset the equilibrium of most of the Weber elements. The old model was defective because in it a narrow range of stable deflection could be secured only by placing the magnets so close together that their stability became far too great. Its quantitative failure in this respect was made apparent by considering the magnitude of the field required to break up pairs or rows of pivoted magnets. In the new model a narrow range of stable deflection is secured without excessive stability. This is because the model is so devised that the control of the Weber element in each atom depends on a slight inequality between strong opposing forces. These forces are exerted separately on different parts of it by other constituents of the atom. Examples of models satisfying this condition are described, with the equivalents of both large and small electron orbits, which reproduce the known characteristics of ferromagnetic induction.

[December 14, 1921.—It is important to notice that the limit of stable deflection for a magnet pivoted as in fig. 1 between closely adjoining fixed poles is determined simply by the closeness of the poles, and is independent of their absolute or relative strengths. Let O,

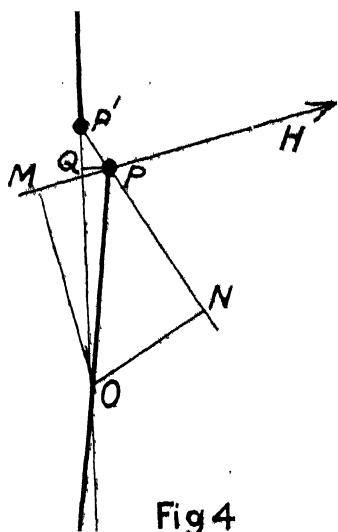


Fig 4

fig. 4, be the centre about which the pivoted magnet turns, P be one of its poles, and P' be the adjoining fixed pole. Let  $m$  be the pole strength of P and let  $m'$  and  $m''$  be the respective pole strengths of P' and its opposite neighbour. Assume that the same geometrical conditions hold at both ends of the pivoted magnet. Suppose a field, H, to act, with a constant inclination  $\alpha$  to the line of centres, OP', with the result of deflecting the pivoted magnet through a small angle QOP or  $\theta$ . Write  $r$  for OP, the half length of the pivoted magnet,  $a$  for OP',

$x$  for PQ, and  $c$  for PP'. The deflecting moment due to the action of H on P is  $mH \cdot OM = mHr \sin(\alpha - \theta)$ . The restoring moment due to the action of P' on P is

$$\frac{mm'}{c^2} \cdot ON = \frac{mm'ax}{c^2},$$

Equating deflecting and restoring moments, we have

$$2mHr \sin(\alpha - \theta) = \frac{m(m' - m'')ax}{c^3}.$$

When  $H$  is increased the limit of stable deflection is found by writing

$$\frac{d}{dx} \cdot \frac{x}{c^3 \sin(\alpha - \theta)} = 0.$$

We are concerned only with very small limiting values of  $\theta$  and it will simplify the expression if we confine it to cases in which  $\sin(\alpha - \theta)$  may be treated as sensibly equal to  $\sin \alpha$ , and therefore sensibly constant, namely cases in which  $\theta$  is very small and  $\alpha$  is not small. Then the criterion for the rupture of stability becomes

$$\frac{d}{dx} \left( \frac{x}{c^3} \right) = 0,$$

which gives  $x = (a - r)/\sqrt{2}$ , since  $c^2 = x^2 + (a - r)^2$ . In other words the deflection ceases to be stable when the angle  $OP'P$  increases to  $\tan^{-1} 1/\sqrt{2}$  or  $35^\circ 16'$ . This is a purely geometrical criterion: it is independent of the magnitudes of  $m$  and of the fixed poles. In the calculation we have assumed the distances of the fixed poles to be the same at both ends of the pivoted magnet, but the stability may be adjusted to any desired value by making the attracting fixed pole stronger than the repelling fixed pole. Thus a narrow range of stable deflection may be retained even when the control is made vanishingly small by having the fixed poles at both ends approach equality in strength as well as distance.

These considerations suggest a further point. Imagine a continuous row of model atoms with fixed magnets lying in one straight line, and in which the opposite fixed poles  $P'$  and  $P''$  are in fact equal and spaced at equal distances from the adjoining moving poles  $P$  and  $-P$ . Though in each atom of the row the action of one fixed pole on the pivoted magnet exactly balances that of the other, there will still be some control, for the pivoted magnets will act on one another as they acted in my model of 1890, but across the intervening gap formed by the outer portions of contiguous atoms. Imagine now a model crystal made up of such atoms. The pivoted magnets will tend to form rows in which the fixed magnets of the intervening gap will also be members. In any one row half the number of fixed magnets will point one way and half the other, but the pivoted magnets will all point one way. Owing to the relatively great distance that separates each pivoted magnet from its nearest pivoted neighbours, the control that is due to the mutual forces between the pivoted magnets will

be very weak ; but since there is (by hypothesis) a nice balance between the forces exerted by the opposing fixed poles, the mutual forces between the pivoted magnets become the operative factor in producing residual magnetism and the other phenomena of hysteresis. The action in the new model would then resemble that of my model of 1890, but with this fundamental difference, that in the new model the mutual forces between the pivoted magnets are exerted across a wide gap, and in that gap there are fixed magnets whose effect is to make the range of stable deflection very narrow, although they do not themselves provide the control which determines the direction the pivoted magnets will assume.

It is at least open to conjecture that in an ideal crystal of perfectly pure and perfectly unstrained iron, what I have called the fixed magnets in each atom may be completely symmetrical and rigid in maintaining their symmetry, while the Weber element turns. In that case the mutual directing forces exerted by the Weber elements on one another, from atom to atom, might still provide the small amount of stability that is required when superposed on the far stronger but balanced forces which are due to the fixed magnets. When, however, the iron is impure, or is rendered æolotropic by straining, it is natural to suppose that each atom is more or less distorted ; in any case the balance of magnetic forces within it is disturbed, and a stronger type of control, due to unequal action on the part of the fixed magnets, is brought into play.]

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*A Contribution to the Thermodynamical Theory of Explosions.*—  
PARTS I AND II.

By Sir J. B. HENDERSON, D.Sc. and Prof. H. R. HASSÉ, D.Sc.

(Communicated by Sir J. A. Ewing, F.R.S. Received May 6, 1921.)

*Introduction.*

The following paper deals with the application of the fundamental ideas of modern physical chemistry to the science of internal ballistics, and aims at eliminating some of the empirical methods and the arbitrary assumptions which have been necessary in the practice and theory of that science in the past. The object of the science is the calculation of the pressure and temperature of the products of explosion throughout the motion of the projectile along the bore of the gun, both during the burning of the propellant and after the burning is completed. It is necessarily a branch of physical chemistry, since it implies a knowledge of the composition of the products of explosion and the variation of these products with temperature, also a knowledge of the variation of the specific heats of gases with temperature. Hence every advance in our knowledge of these branches of physical chemistry will enable a further step to be made in the science of internal ballistics.

To cover our ignorance in this respect it has been customary in internal ballistics to make arbitrary assumptions as to the connection between pressure and volume behind the projectile in the gun. The assumption made for example by Mansell and Haddock\* is that the equation,  $p(v-b)^n/z^n = \text{constant}$ , is satisfied, the value of  $n$  being different during burning and after burning is completed,  $z$  being the fraction of the charge already burnt.

The present paper makes no assumption of this kind, but contains an application to the problems of internal ballistics of the recent advances in the thermodynamics of dissociation and in the thermodynamics of the variation of specific heats of gases with temperature, with the result that the whole indicator diagram of the gun can now be calculated from the chemical composition of the propellant, combined with a table of heats of formation from the elements of the propellant and its products, and one set of laboratory experiments to determine the rate of burning of the solid propellant and its variation with pressure. Physical chemistry is not yet sufficiently advanced to enable this rate to be calculated.

Part I contains the calculations of the maximum temperature and pressure

\* A good review of previous work is given by Sir George Haddock, F.R.S., in his paper on Internal Ballistics, 'Roy. Soc. Proc., A, vol. 94 (1917).



for an explosion in a closed vessel, also the calculation of the curve of reversible adiabatic expansion of the products and incidentally the ideal indicator diagram. This part was written in 1913-14 and publication was then prohibited.

Part II was written in 1915-16 and contains the calculations for the gun, in which the variation with time of the volume of the chamber, of the composition of the products and of the temperature and pressure of explosion, are all worked out point by point and the value of the maximum pressure is determined.

This complete theory was put to very severe test by application to many practical problems during the War, made by that distinguished scientific artillerist, Captain Maxwell Lefroy, R.N., member of the Ordnance Committee, with very satisfactory agreement between theory and practice. Incidentally it may be noted that since actual direct experiments on specific heats of gases have been limited to temperatures below  $1500^{\circ}\text{C}$ . and pressures of a few hundred pounds per square inch, whereas in ballistics temperatures of  $3500^{\circ}\text{C}$ . and pressures of 20 Tons/in.<sup>2</sup> are common, the application to ballistics of the theoretical thermodynamical equations forms a severe test of the theory.

PART I.—*The Calculation of the Temperature of Explosion, the Curve of Adiabatic Expansion, with Special Reference to the Explosion of Cordite and the Ideal Indicator Diagram.\**

By Sir J. B. HENDERSON, D.Sc.

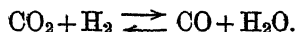
The general theory will be illustrated by an example of its application to the explosion of Mark I. cordite, and the results for M.D. cordite are added, but it will be understood that the method is equally applicable to any propellant.

$$\left. \begin{array}{l} 1 \text{ gm. of} \\ \text{Mark I.} \\ \text{cordite} \end{array} \right\} = \left\{ \begin{array}{l} 0.37 \text{ gm. gun-cotton} \\ 0.58 \text{ " nitroglycerine} \\ 0.05 \text{ " vaseline} \end{array} \right. = \left\{ \begin{array}{l} 0.2808 \text{ gm. carbon} \\ 0.0300 \text{ " hydrogen} \\ 0.1553 \text{ " nitrogen} \\ 0.5837 \text{ " oxygen} \end{array} \right. = \left\{ \begin{array}{l} 0.01924 \text{ gm. atom of C,} \\ 0.0300 \text{ " " " H,} \\ 0.0111 \text{ " " " N,} \\ 0.0365 \text{ " " " O.} \end{array} \right.$$

The products of explosion will contain  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  with possibly small quantities of  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{NO}$ ; it is also possible that some of the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are dissociated, but whatever the composition, it will be assumed that at any temperature the composition represents a state of thermodynamic equilibrium so that the equations for such a state are applicable. We shall first of all neglect the small quantities of  $\text{NH}_3$ ,  $\text{CH}_4$  and  $\text{NO}$  present, also the dissociation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and prove later that these are negligible. The

\* The author is much indebted for valuable assistance and advice on the chemical side to Dr. Thomas Ewan, of Glasgow.

gaseous reaction which varies with the temperature is then the water-gas reaction



Let  $p, q, r$  and  $s$  be respectively the numbers of gramme-molecules per gramme of products, and let C, O, H and N be the numbers of gramme-atoms of C, O, H and N respectively in the products, then

$$p + q = \text{C}; \quad 2p + q = \text{O}; \quad 2r + 2s = \text{H}; \quad \frac{q^s}{p^r} = K_c,$$

where

$$K_c = \frac{[\text{CO}] \times [\text{H}_2\text{O}]}{[\text{CO}_2] \times [\text{H}_2]}.$$

Values of  $\log K_c$  for the water-gas reaction may be obtained from works on physical chemistry.

Since  $K_c$  varies with temperature, it is necessary to assume first of all a value of  $K_c$ , then solve for  $p, q, r$  and  $s$ , and if the values so obtained lead to a value of the temperature considerably different from that associated with the assumed value of  $K_c$ , then the calculations have to be repeated with a new corrected value of  $K_c$ . A large error in  $K_c$ , however, makes a small difference in the products.

Taking  $K_c = 14$  which corresponds to a temperature of  $3400^\circ$  abs.

$p$	=	0.00486	grm.-mols.	per	grm.	cordite.
$q$	=	0.01438	"	"	"	"
$r$	=	0.00262	"	"	"	"
$s$	=	0.01238	"	"	"	"
$N_2$	=	0.00554	"	"	"	"
Sum		=	0.03978	"	"	"

The characteristic equation for a gas, or mixture of gases, at high temperatures and pressures is  $p(v-b) = R\theta$ , where  $v$  is the specific volume of the products,  $b$  the specific volume of the molecules themselves, which may be taken as the specific volume of the solid explosive. The value of  $R$  for a mixture of gases is the sum of the concentrations of the constituent gases in gramme-molecules per gramme, multiplied by a constant which is 2760 ft. Lbs./ lb.  $\times$  deg. C. Hence

$$R = 0.0398 \times 2760 = 109.8 \frac{\text{ft. Lbs.}}{\text{lb.} \times \text{deg. C.}} = 3.25 \frac{\text{atmos.} \times \text{cm.}^3}{\text{gm.} \times \text{deg. C.}}$$

#### *Thermal Values.*

Berthelot has given the heats of formation from the elements of collodion, uncotton, nitroglycerine, vaseline and all the above gases formed in the

explosion, all at 15° C. The heat evolved per gramme of cordite at 15° C. is next calculated from Berthelot's figures combined with the above values of  $p$ ,  $q$ ,  $r$ , etc., which corresponds to the heat evolved in the explosion, or the heat evolved if the gases were cooled from explosion temperature to 15° C. without altering their composition.

	Molecular weight.	Heat of formation per grm.-mol. from elements (at 15° C.).	Heat of formation per grm.
		cal.	
Collodion, $C_{24}H_{31}O_{28}N_9$ .....	1053	696,000	660
Guncotton, $C_{24}H_{29}O_{42}N_{11}$ .....	1143	624,000	546
Nitroglycerine, $C_3H_5N_3O_9$ .....	227	98,000	432
Vaseline, $C_{27}H_{48}(?)$ .....	282	97,100	344
Carbon dioxide, $CO_2$ .....	44	94,300	
Carbon monoxide, $CO$ .....	28	26,300	
Steam, $H_2O$ .....	18	58,000	
Water, $H_2O$ .....	18	68,400	

Since the heats of formation are determined at atmospheric pressure, it is necessary, in order to get the heat of formation  $Q_1$  at constant volume, to add the energy which has been expended in doing external work, namely, 550 calories per gramme-molecule of gas produced. Instead of adding this to each item, it will be added at the end of the heat balance.

Hence the heat balance of the explosion of cordite, Mark I, stands as follows, assuming guncotton to be a mixture of 70 per cent. guncotton,  $C_{24}H_{29}N_{11}O_{42}$  and 30 per cent. collodion  $C_{24}H_{31}N_9O_{38}$  :—

Heat absorbed by the decomposition at 15° C. of—

$$0.7 \times 0.37 \text{ grm. guncotton} = 546 \times 0.259 = 141.4 \text{ cal.}$$

$$0.3 \times 0.37 \text{ „ collodion} = 660 \times 0.111 = 73.3 \text{ „}$$

$$0.58 \text{ grm. nitroglycerine} = 432 \times 0.58 = 250.5 \text{ „}$$

$$0.05 \text{ „ vaseline} = 344 \times 0.05 = 17.2 \text{ „}$$

$$\text{Sum} = 482.4 \text{ cal.}$$

Heat evolved by the formation at 15° C. of—

$$0.00486 \text{ grm.-mol. } CO_2 = 0.00486 \times 94300 = 458.4 \text{ cal.}$$

$$0.01438 \text{ „ } CO = 0.01438 \times 26300 = 378.2 \text{ „}$$

$$0.01238 \text{ „ steam} = 0.01238 \times 58000 = 718.5 \text{ „}$$

$$0.0398 \text{ „ of gas} = 0.0398 \times 550 = 21.9 \text{ „}$$

$$\text{Sum} = 1577.0 \text{ cal.}$$

Hence the total heat evolved per gramme of cordite = 1094.6 cal.

The heat evolved in cooling the gases from explosion temperature to 15° C. must be equal to 1094·6 calories, whence the temperature of explosion is obtainable if the specific heats of the products are known.

### Specific Heats.

Experimental determination of the specific heats of gases by direct measurement is limited to temperatures below 1500° C., and without a thermodynamic theory of the variation of the specific heats with temperature, further advance in the theory of explosion would be difficult, if not impossible. Such theories are those proposed by Einstein and by Nernst and Lindemann, based upon Planck's quantum theory.

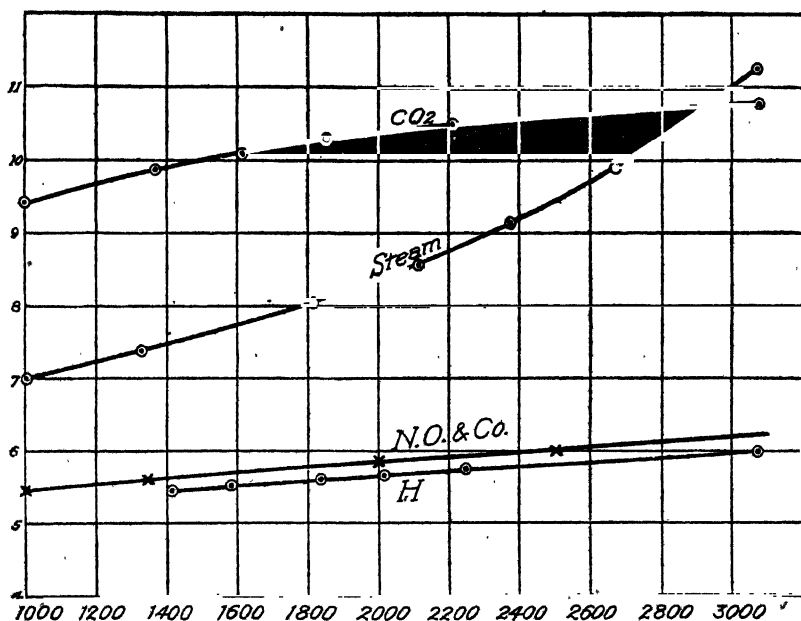


FIG. 1

The curves in fig. 1 show the variation of the specific heats of CO<sub>2</sub>, H<sub>2</sub>O, N, O and H, with temperature as given by Bjerrum, calculated by the Nernst-Lindemann formula

$$\frac{\partial E}{\partial \theta} = \frac{R}{2} \left\{ \frac{x^2 e^x}{(e^x - 1)^2} + \frac{(x/2)^2 e^{x/2}}{(e^{x/2} - 1)^2} \right\} \text{ where } x = \frac{hn}{R\theta}$$

The following table is prepared from these curves :—

Grm.-mol. of products per grm. of cordite.	$t = 2000^{\circ} \text{C.}$		$t = 2500^{\circ} \text{C.}$		$t = 3000^{\circ} \text{C.}$	
	Mol. heat.	Mol. heat $\times$ grm.-mol. of products.	Mol. heat.	Mol. heat $\times$ grm.-mol. of products.	Mol. heat.	Mol. heat $\times$ grm.-mol. of products.
$\text{CO}_2 = 0\cdot00486$ .....	10·32	0·0501	10·57	0·0514	10·75	0·0528
$\text{CO} + \text{N}_2 = 0\cdot01992$ ...	5·77	0·1150	5·94	0·1184	6·15	0·1226
$\text{H}_2 = 0\cdot00262$ .....	5·62	0·0147	5·78	0·0151	5·95	0·0156
$\text{H}_2\text{O} = 0\cdot01238$ .....	8·42	0·1042	9·46	0·1171	11·02	0·1365
Heat capacity of products =		0·2840	—	0·3020	—	0·3270

Now, the product heat capacity  $\times$  temperature = heat contents, and the temperature has to be calculated at which this product is equal to the heat evolved in the explosion, namely, 1094·6 calories per gramme of cordite.

Temperature.	Heat capacity.	Product.	Difference.
2000	0·2840	568	—
2500	0·3020	755	187
3000	0·3270	981	226

Plotting the product on a temperature base and reading off the temperature corresponding to a product 1095, we find  $3210^{\circ} \text{C.}$ , or  $3483^{\circ}$  absolute.

In Service Chemistry a simple approximate formula is given for Mark I. cordite:— $\text{C}_5\text{H}_8\text{N}_3\text{O}_{10}$ . If the above calculations are repeated, using this formula the results are:— $p = 0\cdot00572$ ,  $q = 0\cdot01278$ ,  $r = 0\cdot00202$ ,  $s = 0\cdot01278$ ,  $\text{N}_2 = 0\cdot00556$  and  $R = 3\cdot175$ . The heat evolved by the formation of the products = 1638·2, and, assuming the heat absorbed by the decomposition of the cordite molecule the same as above, viz., 482, the heat balance is 1156·2 and the temperature of explosion is  $3600^{\circ} \text{C.}$  absolute, instead of  $3500^{\circ}$  from Berthelot's composition formulæ.

The calculations have also been repeated for M.D. cordite, containing 65 per cent. guncotton, 30 per cent. nitro-glycerine, and 5 per cent. vaseline, with the following results:— $p = 0\cdot0031$ ,  $q = 0\cdot0184$ ,  $r = 0\cdot0046$ ,  $s = 0\cdot0111$ ,  $\text{N}_2 = 0\cdot0050$ , Sum =  $0\cdot0422$ ,  $R = 3\cdot44$  (atmos.  $\times$  cm.<sup>3</sup>)/grm.  $\times$  deg. C.). The heat of formation of 1 grm. of M.D. cordite is 524, and the heat balance works out at 913 calories evolved per gramme; and the temperature of explosion is  $2870^{\circ} \text{C.}$ , or  $3143^{\circ} \text{C.}$  absolute, or  $340^{\circ} \text{C.}$  lower than for Mark I.

*Influence of Initial Temperature of Cordite.*

The influence of the initial temperature may be determined as follows :— Let the explosion take place at different initial temperatures,  $t_1$  and  $t_2$ , the corresponding temperatures of explosion being  $T_1$  and  $T_2$ . It is easy to imagine the chemical change taking place at  $t_1$  until the products are the same as exist at  $T_1$ , and that the products are then heated up from  $t_1$  to  $T_1$  by the heat evolved. Secondly, imagine that the cordite is heated up from  $t_1$  to  $t_2$  by adding heat  $h$  from external sources, then let the chemical change take place at  $t_2$  until the products are those existing at  $T_2$ , the heat evolved being then used to raise the temperature of the products from  $t_2$  to  $T_2$ . If the heat  $h$  were not supplied from external sources, the final temperature in the second case must be  $T_1$ , since the temperature of explosion is independent of the path followed in the explosion. Hence the heat  $h$  is equal to that required to raise the temperature of the products from  $T_1$  to  $T_2$ , neglecting the small difference in the products at these temperatures, so that

$$\begin{aligned} &(\text{specific heat of solid cordite}) (t_2 - t_1) \\ &= (\text{specific heat of products at constant volume at} \\ &\quad \text{temperature of explosion}) (T_2 - T_1). \end{aligned}$$

Now, the specific heats of solid cordite at ordinary temperatures are 0.365 for Mark I. and 0.347 for M.D., as given by Sir Robert Robertson, and, for the former, the specific heat of the products at the temperature of explosion is 0.372, as calculated from the above theory. Hence the rise in the temperature of explosion is  $0.365/0.372$  of the rise in the temperature of the solid cordite, so that the temperature of explosion is practically increased by an amount equal to the rise of temperature of the solid cordite. For an increase from  $60^\circ$  F. to  $80^\circ$  F., the temperature of explosion is therefore increased by  $20^\circ$  F., or  $11^\circ$  C., which is within the limits of error in the determination of the temperature of explosion itself.

*Pressure of Explosion.*

The temperature of explosion having been determined, the pressure for any particular density of loading follows at once from the characteristic equation. For Mark I. cordite,  $b = 0.641$  cm.<sup>3</sup>/grm., and, if the density of loading be 0.5 grm. per cm.<sup>3</sup> of bomb capacity,

$$p = 8370 \text{ atmos.} = 55.1 \text{ tons/in}^2.$$

*Correction of Results for Dissociation.—Dissociation of CO<sub>2</sub> at 3500° abs. and Pressure of Explosion.*

$$\log_{10} K_d = \log_{10} \frac{[\text{CO}]^2 [\text{O}_2]}{[\text{CO}_2]^2} = -1.6 = \bar{2}.40.$$

With a density of loading 0.5 grm./cm<sup>3</sup>, or 1 grm. per 0.002 litre, the concentrations are at once determined by the composition of the products on p. 463.

$$[\text{CO}_2] = \frac{0.00486}{0.002} = 2.43 \text{ grm.-mols./litre,}$$

$$[\text{CO}] = \frac{0.01438}{0.002} = 7.19 \quad \text{,,} \quad \text{,,}$$

whence  $[\text{O}_2] = 0.00287$ , or 0.0012 grm.-mols. of O<sub>2</sub> per gramme-molecule of CO<sub>2</sub>, and since the dissociation of 2 grm.-mols. of CO<sub>2</sub> give 1 grm.-mol. of O<sub>2</sub>, the percentage of CO<sub>2</sub> dissociated is 0.24. If the density of loading were 0.05 the percentage dissociated would be 2.4.

*Dissociation of Steam.*—Dealing with the H<sub>2</sub>O in a similar manner and taking  $\log K_e = 5.97$ , gives 0.06 as the percentage H<sub>2</sub>O dissociated at a density of loading of 0.5, which is negligible.

In a similar manner we get  $[\text{CH}_4] = 1.3 \times 10^{-6}$  which is negligible. CH<sub>4</sub> is formed in cooling the products.

$$[\text{NO}] = 0.0160 \text{ grm.-mols. per litre.}$$

$$= 32 \times 10^{-6} \text{ grm.-mols. per gramme cordite.}$$

$$= 0.96 \text{ per cent. of the products of decomposition.}$$

$$[\text{NH}_3] = 0.41 \text{ grm.-mols./litre.}$$

$$= 0.00082 \text{ grm.-mols. per gramme of cordite.}$$

$$= 1.4 \text{ per cent. of the products of decomposition.}$$

All these are very small as compared with the main products, CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>, and are *negligible where an accuracy* of about 1 per cent. is aimed at. If any of them were not negligible, it would be easy to allow for it by successive approximation.

*Heat Contents of the Products of Explosion and Curve of Adiabatic Explosion.*

The composition of the products, if in chemical equilibrium, depends only on the temperature, and the intrinsic energy in each of the constituents depends also only on the temperature, hence the heat contents of the products of explosion is a function of the temperature only. It is therefore necessary to take an arbitrary datum both for temperature and for composition of products. The datum taken for temperature is 0° C. and the datum for composition is conveniently taken as the composition at 1500° C. abs.

The heat contents is, therefore, the heat evolved in cooling the products to 1500° abs., allowing combination to take place, and then cooling the products further to 0° C. without allowing further combinations to take place. It will be more convenient in tabular work to cool the products to 0° C. without allowing combination to take place and then allow the product to combine at 0° C. until the composition is that corresponding to 1500° abs. The result must be independent of the path followed, since it is a function of the temperature only.

In Table I the composition of the products of Mark I. cordite is given at 1500°, 2000°, 2500°, 3000°, and 3500° abs., each column being calculated by the method given on p. 463. The heat of reaction for water-gas is added, and these figures might be used if the products were imagined to combine at these temperatures to the standard composition before being cooled to 0° C. They are added chiefly to show that a maximum heat of reaction exists at about 2000° abs. This maximum must have a considerable effect in influencing the final composition of the products formed in bomb calorimeters. The heat of reaction at 0° C. is 10,420 calories per gramme-molecule, and its value at any other temperature  $t$  is obtained from the equation

$$Q + t \text{ (mean specific heat of products)} \\ = Q_0 + t \text{ (mean specific heat of the combining gases).}$$

Table I.—Composition of the Products of Combustion of Mark I. Cordite at various Temperatures.

Temp. deg. C. ....	1227°	1727°	2227°	2727°	3227°
Temp. abs. ....	1500°	2000°	2500°	3000°	3500°
K <sub>c</sub> .....	3·71	6·61	9·5	12·6	16·2
CO <sub>2</sub> .....	0·00700	0·00600	0·00542	0·00502	0·00467
CO .....	0·01224	0·01324	0·01382	0·01422	0·01457
H <sub>2</sub> .....	0·00476	0·00376	0·00318	0·00278	0·00243
Steam .....	0·01024	0·01124	0·01182	0·01222	0·01257
N <sub>2</sub> .....	0·00554	0·00554	0·00554	0·00554	0·00554
Sum .....	0·03978	0·03978	0·03978	0·03978	0·03978
Heat of reaction .....	13,842	14,082	13,717	11,866	6,548

Table II contains the results of the calculation of the heat capacity of the products of explosion of Mark I. cordite, the datum of reference being the



Table II.—Heat Capacity of the Products of Explosion of Mark I Cordite, the Datum of Reference being the Products at 1500° absolute cooled to 0° C.

	1500° abs. = 1227° C.			2000° abs. = 1727° C.			2500° abs. = 2227° C.			3000° abs. = 2727° C.			3500° abs. = 3227° C.			
	Grm.-mols. per grm. of products.	$k_m^*$ 0°- $t^{\circ}$ C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°- $t^{\circ}$ C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°- $t^{\circ}$ C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°- $t^{\circ}$ C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°- $t^{\circ}$ C.	Heat contents due to cooling.	
CO <sub>2</sub> ...	0·00700	9·69	83·2	0·00600	10·16	105·2	0·00542	10·46	126·3	0·00502	10·7	146·5	0·00467	10·8	162·8	
N <sub>2</sub> +CO	0·01778	5·46	119·2	0·01878	5·64	182·6	0·01986	5·83	251·5	0·01976	6·02	324·5	0·02011	6·24	405·1	
H <sub>2</sub> ...	0·00476	5·30	31·0	0·00376	5·50	35·7	0·00318	5·63	40·2	0·00278	5·90	44·7	0·00243	6·10	47·8	
H <sub>2</sub> O ...	0·01024	7·16	90·0	0·01124	7·9	153·3	0·01182	8·84	232·8	0·01222	10·1	336·7	0·01257	11·9	430·0	
Heat contents due to cooling.	323·4		476·8		650·8		852·4		1097·7		1397·7		1697·7		1997·7	
Heat contents due to chemical change	0		10420 × 0·0010 = 10·4		10420 × 0·00158 = 16·5		10420 × 0·00198 = 20·6		10420 × 0·00233 = 24·3		10420 × 0·00268 = 28·3		10420 × 0·00303 = 32·3		10420 × 0·00338 = 36·3	
Total heat contents above 0° C.	323·4		487·2		667·3		873·0		1072·0		1272·0		1472·0		1672·0	

\*  $k_m$  is the mean specific heat between 0° and  $t^{\circ}$  C.

Table III.—Heat Capacity of the Products of Explosion of M.D. Cordite, the Datum of Reference being the Products at 1500° absolute cooled to 0° C.

	1500° abs. = 1227° C.			2000° abs. = 1727° C.			2500° abs. = 2227° C.			3000° abs. = 2727° C.			3500° abs. = 3227° C.		
	Grm.-mols. per grm. of products.	$k_m$ 0°-f° C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°-f° C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°-f° C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°-f° C.	Heat contents due to cooling.	Grm.-mols. per grm. of products.	$k_m$ 0°-f° C.	Heat contents due to cooling.
CO <sub>2</sub> ...	0·00543	9·69	64·56	0·00434	10·16	76·10	0·00372	10·46	86·66	0·00323	10·7	94·24	0·00291	10·8	101·40
N <sub>2</sub> + CO	0·02108	5·46	141·22	0·02217	5·64	215·90	0·02279	5·83	235·95	0·02328	6·02	382·20	0·02360	6·24	475·20
H <sub>2</sub> ...	0·00896	5·30	45·26	0·00887	5·50	55·74	0·00825	5·68	66·41	0·00476	5·90	76·60	0·00444	6·10	87·40
H <sub>2</sub> O ...	0·00871	7·16	76·52	0·00880	7·90	133·65	0·01042	8·84	205·20	0·01091	10·10	300·50	0·01123	11·9	432·10
Heat contents due to cooling			327·56			481·89			654·22			853·54			1096·10
Heat contents due to chemical change			0	10420 × 0·00109 =		11·36	10420 × 0·00171 =		17·82	10420 × 0·00220 =		22·92	10420 × 0·00252 =		26·26
Total heat contents.....			327·56			492·75			672·04			876·46			1122·36

products at 1500° abs., cooled to 0° C. The total heat contents given in the last line of the Table are represented within 1 per cent. by the equation

$$H = 15.2 + 0.1223\theta + 55.4 \times 10^{-6}\theta^2$$

where H is in calories per gramme of products of explosion.

Table III corresponds to Table II, but refers to M.D. cordite.

### *Adiabatic Expansion.*

The equation for a reversible adiabatic expansion expresses the fact that the loss of intrinsic energy is equal to the external work done, or

$$p\delta v = -\left(\frac{\partial H}{\partial \theta}\right)\delta\theta = -(0.1223 + 110.8 \times 10^{-6}\theta)\delta\theta,$$

and since  $p(v-b) = R\theta$  it follows

$$\frac{dv}{v-b} = -\frac{d\theta}{R\theta}(0.1223 + 110.8 \times 10^{-6}\theta)$$

whence  $\log_e \frac{v-b}{v_1-b} = \frac{0.1223}{R} \log_e \frac{\theta_1}{\theta} + \frac{110.8 \times 10^{-6}}{R}(\theta_1 - \theta),$

and substituting the values for R we get

$$\log_{10} \frac{v-b}{v_1-b} = 1.552 \log_{10} \frac{\theta_1}{\theta} + 617 \times 10^{-6}(\theta_1 - \theta),$$

which is the equation for adiabatic expansion. It is easily shown that this equation cannot be represented with sufficient accuracy by an equation of the form  $p(v-b)^n = \text{constant}$ , which necessarily involves H being a linear function of  $\theta$ , whereas it is a quadratic function. This latter type of equation could be used for small changes of temperature,  $n$  varying with the temperature according to

$$\frac{R}{n-1} = \frac{dH}{d\theta} = 0.1223 + 110.8 \times 10^{-6}\theta.$$

### *Results for M.D. Cordite.*

$$H = 14.68 + 0.1323\theta + 52.57 \times 10^{-6}\theta^2.$$

$$R = 3.486 \times 10^{-6} \text{ ergs./gram.} \times \text{deg. C.}$$

$$= 0.0831 \text{ gram. cal./gram.} \times \text{deg. C.}$$

Adiabatic expansion is given by

$$\log_{10} \frac{v-b}{v_1-b} = 1.593 \log \frac{\theta_1}{\theta} + 549 \times 10^{-6}(\theta_1 - \theta).$$

Heat balance = 913 cal./gram.; temperature of explosion = 2870° C. or 340° lower than Mark I.

*Ideal Indicator Diagram and Mechanical Efficiency of a Gun.*

The ideal indicator diagram may be considered as that obtained by a sudden explosion of all the propellant before the projectile begins to move, to be followed by an adiabatic expansion of the products. The maximum pressure obtained in this way is much greater than the gun could stand; hence it is fairer to take the ideal as that obtained by burning the propellant at the maximum working pressure for which the gun is designed, to be followed by adiabatic expansion.

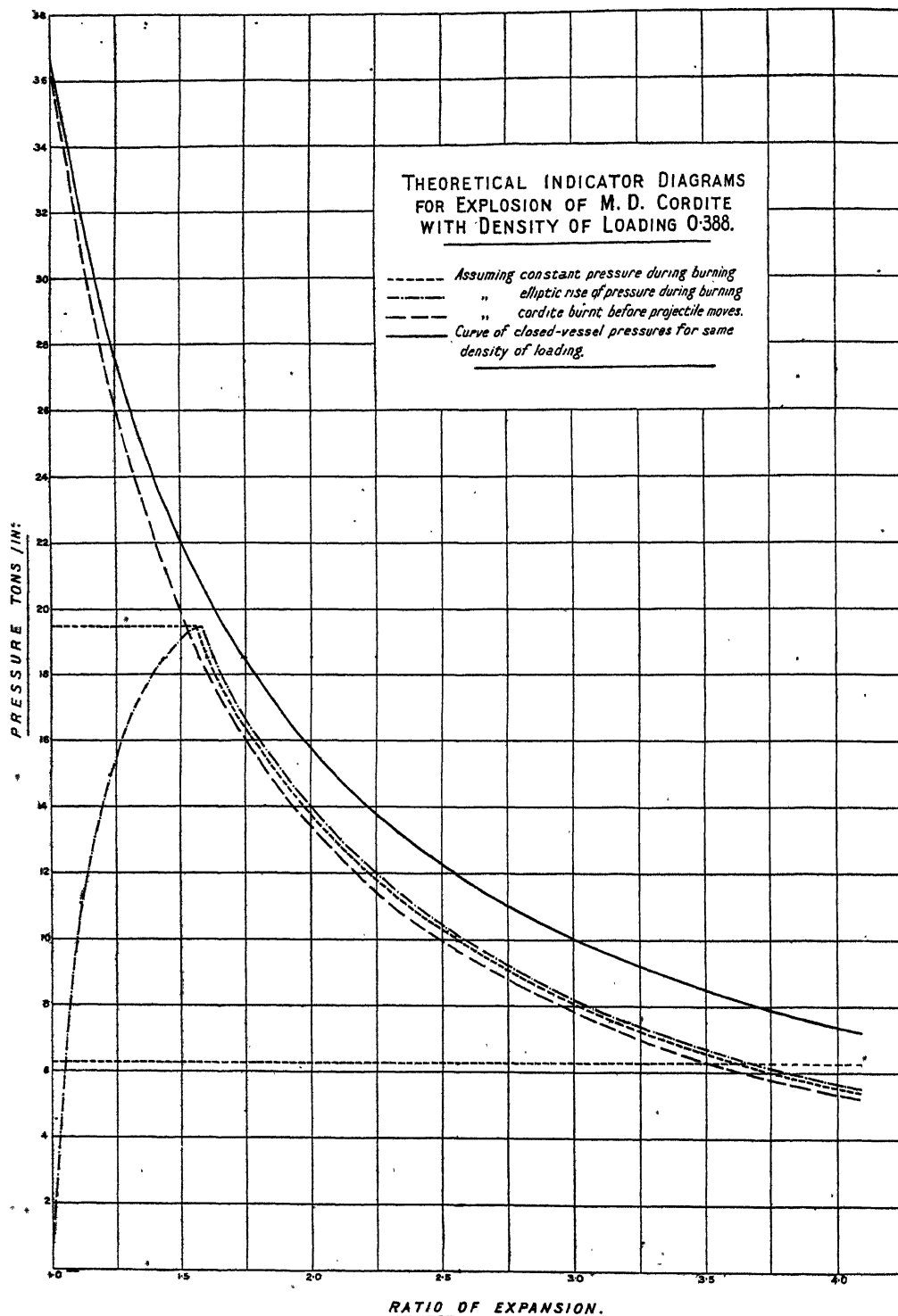
Fig. 2 shows both types of ideal indicator diagram for M.D. cordite, and, in addition, the curve of pressures for irreversible adiabatic expansion, as in throttling, in which no work is done, corresponding to explosions in closed vessels of different capacities; also the ideal indicator diagram assuming an elliptic curve of rise of pressure; also the uniform pressure at which the cordite would just be all burnt at the muzzle of a gun having a ratio of expansion  $v/v_0$  equal to 4.09.

*Mechanical Efficiency of the Gun.*

Taking the mechanical efficiency of a gun as the ratio of the sum of the kinetic energies of the projectile as it leaves the muzzle, due to translation and rotation, to the work represented by the area of the ideal indicator diagram, as calculated above, the following Table is evolved:—

Table of Efficiencies (M.D. Cordite).

Gun.	Density of loading.	Mass of charge.	$V/V_0$ .	Ballistics (experimental).		Thermodynamical work.	Total energy of projectile.	Efficiency.
				Maximum pressure.	Muzzle velocity.			
		lbs.		Tons/ins. <sup>2</sup>	ft./sec.	ft. Tons.	ft. Tons.	per cent.
6" Mark VII ...	0.463	23½	4.986	16.55	2761	6,237	5,315	85.2
7.5" Mark III...	0.404	54½	4.993	17.79	2781	12,400	10,790	87.0
9.2" Mark XI	0.396	128½	3.990	17.76	2870	25,990	21,320	84.0
12" Mark X .....	0.401	260	3.954	16.29	2735	50,630	44,340	87.6
13.5" Mark V ...	0.419	297	4.850	18.78	2501	67,610	60,970	90.2



PART II.—*The Rate of Rise of Pressure of the Explosion of Cordite in a Gun.—  
The complete Indicator Diagram of the Explosion.*

By Sir J. B. HENDERSON, D.Sc., and Prof. H. R. HASSÉ, D.Sc.

The object of this part of the paper is the application of the results of the thermodynamical theory of Part I to the general problem of Internal Ballistics, the variation of temperature and pressure behind the projectile as it moves along the barrel of a gun. The mathematical theory which follows differs from that given in work previously published,\* in that it is more strictly in accordance with thermodynamical theory; Charbonnier's equations form a special case of the theory, but are not treated in the same way as in the present paper.

The essential features of the theory of Part I of this paper are (1) the determination of the temperature  $\theta_0$  of the explosion; and (2) the expression of the heat contents,  $H$ , of the products of explosion in the form  $\alpha' + \beta'\theta + \gamma'\theta^2$ . The loss of heat contents per unit mass of gas, which measures the work done per unit mass, and is denoted by  $h$ , may therefore be written in the form

$$h = \beta'\theta_0 + \gamma'\theta_0^2 - \beta'\theta - \gamma'\theta^2. \quad (1)$$

For many purposes it is more convenient to express  $\theta_0 - \theta$  as a quadratic function of  $h$ . It is found from (1) that for M.D. cordite the equation

$$\theta_0 - \theta = 3.381h + 20.45 \times 10^{-4}h^2 \quad (1a)$$

will give results in agreement with (1), well within the possible error of (1) as deduced from the theoretical considerations of Part I.

For temperatures differing from that of explosion by less than about  $300^\circ$ ,  $h$  may be expressed as a linear function of  $\theta$  in the form

$$h = f(\theta_0 - \theta), \quad (1b)$$

where for M.D. cordite

$$f = 0.28245 \frac{\text{ft. Tons}}{\text{lb. deg. C.}}$$

*Fundamental Equations of the Theory.*

In formulating these equations, it should be noted: (1) that all forces opposing the motion of the projectile have been neglected; (2) that no attempt has been made to allow for the loss of heat to the walls of the gun; and (3) that it has been assumed that the rate of burning of the propellant depends only on the pressure of the surrounding gas, and is, moreover, proportional to the pressure. The fundamental gas equation is

$$p(V - m_1b) = Rm\theta, \quad (2)$$

\* *E.g.*, the standard work of Charbonnier, 'Balistique Intérieure,' 1908.

$p$  and  $\theta$  being the pressure and temperature of the gas, which has a mass  $m$ ,  $V$  is the volume of the space behind the projectile,  $m_1$  is the total mass of the charge, and  $b$  is the reciprocal of the density of the solid explosive. The theoretical deduction of this equation depends essentially on this interpretation of the constant  $b$ , but the equation may be looked upon as an empirical generalisation of the similar equation, deduced from experimental results in closed vessels, and the value of  $b$  chosen in accordance with these results.\*

If  $M$  is the mass of the projectile,  $u$  its velocity,  $A$  the area of the cross-section of the bore, including that of the grooves, its equation of motion is

$$M \frac{du}{dt} = pA. \quad (3)$$

The scheme of theoretical equations is completed by the equation

$$pdV = d(mh), \quad (4)$$

which expresses the work done by the gases on the projectile in terms of the total loss,  $mh$ , of heat contents at any instant. From these equations, we deduce from (2) and (4) that

$$R \frac{dU}{U} = \frac{d(zh)}{z\theta}, \quad (5)$$

where  $z = m/m_1$ , and is therefore the fraction of the charge burnt at any instant, and  $U \equiv V - m_1 b$ , which may be called the "free volume" behind the projectile.

Again from (3) and (4) it follows that

$$m_1 zh = \frac{1}{2} Mu^2, \quad (6)$$

the equation of energy, as is otherwise obvious.

It is known that any propellant when once ignited is burnt in parallel layers, so that the rate at which the thickness diminishes is, in accordance with the statement made above, given by

$$\frac{de}{dt} = f(p), \quad (7)$$

where  $e$  is the thickness burnt off from any surface in time  $t$ . According to Petavel† and Mansell‡  $f(p)$  for cordite is equal to  $a_0 + a_1 p$ . Using the values given by them, the first term is only of importance for low values of the pressure, i.e., in the initial stages of the explosion, or when the densities of loading are low, when there are other factors of much more importance to be taken into consideration, so that in what follows we shall take  $f(p) = ap$  as

\* Charbonnier, *op. cit.*, pp. 9-17.

† Petavel, 'Phil. Trans.,' A, vol. 205 (1906).

‡ Mansell, 'Phil. Trans.,' A, vol. 207 (1908).

being more applicable to normal gunnery practice, leading to a considerable simplification in the mathematics of the theory. This is also taken to be the law of burning for French propellants by Charbonnier. There is, finally, the relation connecting the thickness  $e$  with the fraction  $z$  of the gas burnt off, which depends upon the geometry of the propellant, and will be discussed later.

It is of interest to consider the connection between this theory and that of Charbonnier. Taking (2) and (6), and considering the particular case in which the loss of heat contents,  $h$ , is proportional to the drop of temperature, as in (1b), we have, on elimination of  $h$  and  $\theta$ ,

$$\frac{1}{2} Mu^2 + \frac{f}{R} p (V - m_1 b) = m_1 f \theta_0 z$$

which is equivalent to Charbonnier's third fundamental equation,\* differing from it only in the interpretation of the constants involved. As obtained by Charbonnier, this equation appears to be an empirical modification of the corresponding equation applying to the case when the cordite is all burnt before the projectile moves, and it is curious that it should turn out to be a special case of the theory of this paper.

#### *Derived Equations for Initial Pressure $p_0$ .*

If it were possible to obtain an expression for the resistance encountered by the projectile during the engraving of the driving band, it would not be difficult to incorporate it into the general theory of this paper, though the resulting differential equations might have to be solved arithmetically. In the absence of such an expression, the influence of the driving band may be discussed by studying the effect produced on the indicator diagram by raising the initial pressure before the projectile begins to move.†

Suppose therefore that the pressure rises to a value  $p_0$  before the projectile moves, a mass  $m_0$  of propellant having been burnt, the equation connecting these two quantities being

$$p_0 = R m_0 \theta_0 / U_0$$

as in the explosion in a vessel of constant capacity  $V_0$ , where  $U_0 = V_0 - m_1 b_1$  and  $V_0$  is the volume of the chamber of the gun. Taking  $f(p) = ap$ , we have from (3) and (7) on integration

$$Mu = \frac{A}{a} (e - e_0), \tag{8}$$

where  $e_0$  is the thickness burnt before the projectile moves.

\* *Op. cit.*, pp. 141, 142.

† This method has been used by Charbonnier and others.



From (6) and (8) we then have

$$zh = \frac{1}{2} \frac{A^2}{m_1 M a^2} (e - e_0)^2 = \frac{1}{2} \frac{A^2 e_1^2}{m_1 M a^2} \left( \frac{e}{e_1} - \frac{e_0}{e_1} \right)^2$$

where  $2e_1$  is the total thickness to be burnt through before the propellant is converted into gas.

Writing  $B = \frac{1}{2} A^2 e_1^2 / m_1 M a^2$  which is the fundamental constant of the theory, and putting  $y = e/e_1$ , so that  $y$  is the fraction of the thickness burnt at any time, the last equation reads

$$zh = B (y - y_0)^2. \quad (9)$$

The geometry of the propellant gives the relation between  $z$  and  $y$  in the form

$$z = \phi(y). \quad (10)$$

Finally from (5) we get

$$R \frac{dU}{U} = \frac{d(zh)}{z\theta} = \frac{2B (y - y_0) dy}{\phi(y) \chi(h)} \quad (11)$$

where we have put  $\theta = \chi(h)$ , being the general form of an equation of the type (1a), and  $h$  is further a function of  $y$  from (9) and (10).

The integration of (11) and its reduction to a form suitable for numerical calculation is the sole mathematical difficulty, and an accurate analytical result can only be obtained in very few cases. For many purposes it will be sufficient to give to the temperature  $\theta$  a mean value  $\bar{\theta}$ , which may be taken as the arithmetic means of the temperatures corresponding to the initial and final values of  $y$ . This gives an approximate integration of (11), which gives very accurate results up to the point of maximum pressure, since the variation of  $\theta$  is small compared with that of  $y$ , in the form

$$R \log (U/U_0) = \frac{2B}{\bar{\theta}} (F_1 - y_0 F_2) \quad (12)$$

where

$$F_1(y) \equiv \int_{y_0}^y \frac{y}{\phi(y)} dy, \quad F_2(y) \equiv \int_{y_0}^y \frac{dy}{\phi(y)}.$$

The form of  $\phi(y)$  has been given for all the ordinary shapes by various writers, and is in general a cubic function of  $y$ ; (*cf.*, *e.g.*, Ingalls, 'Interior Ballistics,' and Charbonnier's work already quoted). In the case of the multi-perforated American nitro-cellulose there is a difficulty when the grain breaks up into the so-called "slivers," which are cylinders whose cross-sections are composed of arcs of circles, and it is not easy to treat these by accurate mathematics. Fortunately, in general about 85 per cent. of the charge is burnt when this break-up occurs, and approximate methods of calculation can be applied to the slivers. In order to avoid any discontinuity in the rate at which the pressure changes, the initial volume *and* surface of the slivers

should agree with the initial volume and surface of the more tractable geometrical form, by which the slivers are replaced for the purpose of the calculation. This makes  $\phi(y)$  and its differential coefficient continuous at the point where the form of the function changes.

*Maximum Pressure of Explosion.*

One of the most important results is the value of the maximum pressure, since this can be determined experimentally, and the comparison of the theoretical and experimental values is of the greatest importance in testing the theory.

By differentiating (2) and using (2) and (4), it will be found that the pressure is a maximum when

$$R \frac{d}{dz}(z\theta) = \frac{d}{dz}(zh). \quad (13)$$

This result can be simplified if we use (1b) instead of (1a) since we expect only a small drop of temperature while the charge is burning rapidly before the maximum pressure is reached. In this case the left-hand side of (13) is

$$R \frac{d}{dz} z(\theta_0 - h/f) = R\theta_0 - \frac{R}{f} \frac{d}{dz}(zh),$$

so that (13) reduces to

$$Rf\theta_0 = (R+f) \frac{d}{dz}(zh), \quad (14)$$

or finally, from (9) and (10) to

$$Rf\theta_0 \frac{d\phi}{dy} = 2B(R+f)(y-y_0). \quad (15)$$

This equation, in general a quadratic in  $y$ , having been solved, the corresponding value of  $h$  is found from (9) and (10), whence  $\theta$  can be calculated from (1b), while the corresponding value of  $U$  is found from (12), so that the maximum pressure is readily determined.

So far the investigation applies only up to the instant at which the cordite is all burnt. After this there is only the expansion of the whole mass of gas to be dealt with and the equation for adiabatic expansion obtained in Part I applies; but if  $h$  is used as independent variable, the equation of adiabatic expansion is from (5), since  $z$  is now unity,

$$R \frac{dU}{U} = \frac{dh}{\theta} = \frac{dh}{\chi(h)},$$

the integration of which can be readily adapted to numerical work in the case of cordite, in which  $\theta$  is given in terms of  $h$  by (1a).

*Results for M.D. Cordite.*

In the case of the standard British propellant, cordite, made up into cylinders assumed so long that the burning at the ends can be neglected,  $\phi(y) = 1 - y^2$ , and (15) is therefore a simple equation for the value of  $y$  at maximum pressure. The actual drop of temperature to maximum pressure can be shown to be always less than  $R\theta_0/2(R+f)$ , which in this case is  $240^\circ$ , a result which justifies the procedure by which, in the calculation of the maximum pressure,  $h$  has been taken to be a linear function of the temperature.

In this case also the integration of (11) can be carried out analytically,  $\theta$  being given in terms of  $h$  from (1a), and the value of  $\log(U_1/U_0)$  can be expressed in terms of  $B$  and  $z_0$ ,  $U_1$  being the value of  $U$  at the instant when the charge is all burnt. For practical purposes it would be necessary to tabulate  $\log(U_1/U_0)$  as a double-entry table in  $B$  and  $z_0$ , but various methods of approximate integration of (11) can be devised, which are sufficiently accurate for the purpose, and which avoid the heavy arithmetical work involved in the calculation of such a table.

As an example, the theory has been applied to the case of an 11-inch gun, using M.D. cordite, for which we may take  $m_1 = 238$  lb.,  $M = 760$  lb.,  $r_1 = 0.15$  in. The value of the constant  $\alpha$  for the rate of burning is taken from Mansell's investigation, and is  $0.611$  in.<sup>3</sup>/Ton-sec. for the charge at  $60^\circ$  F. The initial pressures have been taken as 0, 1, and 2 Tons/in.<sup>2</sup> respectively, and the corresponding indicator diagrams are plotted in fig. 3. They show the effect of raising the initial pressure on both the maximum pressure and on the position of the projectile when the charge is all burnt. It has also, of course, a considerable influence on the total thermo-dynamical work done, which is proportional to the area under the curves, its magnitude for the three cases being 46,590, 47,710, and 48,380 foot-Tons respectively.

The value of the initial pressure,  $p_0$ , which must be taken in order to make the experimental and theoretical maximum pressures agree, depends naturally on the value of the constant  $\alpha$  chosen as the standard, and is usually of the order of 2 to 4 Tons/in.<sup>2</sup>. The value of  $p_0$  having been chosen in this way, it is found that in the largest guns the experimental kinetic energy of the projectile is from 92 to 95 per cent. of the total energy measured in the indicator diagram.

The above statements cannot, of course, apply to all guns and to all charges; they are only approximate, but show the order of magnitude of the empirical factors, which in any form of theory have to be introduced in order

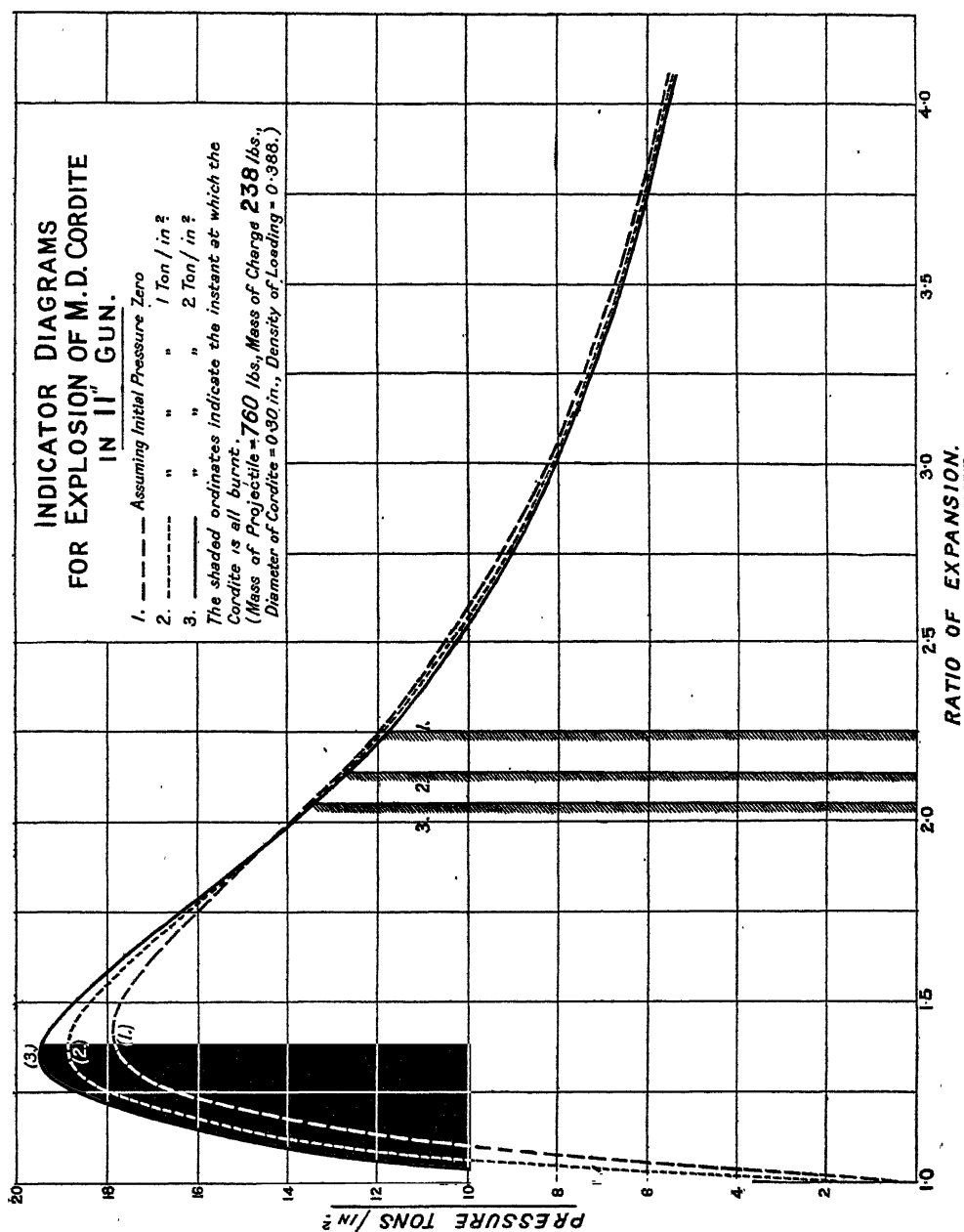


FIG. 3.

to take into account the resistance of the driving band and the losses of energy in heat and friction.

*Equations for Zero Initial Pressure.*

The equations of the theory are considerably simplified if it is assumed that the projectile begins to move directly any gas has been given off from the burning charge. The corresponding equations can easily be found by making  $y_0$  zero in (9), (11), (12), and (15), the whole course of the explosion then depending on the single parameter B.

Applied to any particular case, these equations will always give too low a maximum pressure, but they may be used with a modified interpretation so as to be of practical value. Apart from the constants in the expression for  $h$  as a function of  $\theta$ , there are two other constants,  $\theta_0$  and  $\alpha$ , which appear in the equations. If it be assumed that the frictional force in the rifling can be allowed for by a virtual increase in the mass of the projectile, then it is a simple extension to consider all such forces which give rise to losses of energy as allowed for in this way, which is equivalent to a decrease in the fundamental constant B.

Taking the constants  $\theta_0$  and  $\alpha$ , as determined from theoretical or experimental considerations, we can allow for all neglected losses of energy by finding in what ratio B must be diminished in order, for example, to give the correct maximum pressure. The same ratio—a coefficient of ignorance—may then be used in calculations for a similar type of gun.

This method is essentially that employed by Ingalls in his 'Interior Ballistics.' Ingalls has two disposable constants, corresponding in some ways to the  $\theta_0$  and  $\alpha$  of this theory, and he determines them separately, so as to make the experimental and calculated values of the maximum pressure and muzzle velocity agree. These values can then be employed in future calculations with the same propellant and a similar type of gun.

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*The Specific Heats of Air, Steam and Carbon Dioxide.*

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(Communicated by Sir Dugald Clerk, F.R.S. Received August 30,—Revised November 25, 1921.)

The late Prof. Bertram Hopkinson designed a recording calorimeter for explosions, of which a description has already been given.\* It was hoped, by means of this calorimeter, to measure the apparent specific heats of the mixture of gases expanding in a gas-engine cylinder. A charge of coal-gas and air was exploded in a closed cast-iron vessel, the walls of which were lined with a continuous copper coil. The coil formed one arm of a Wheatstone's bridge, and thus, by the change in resistance of the coil, it was possible to measure the heat passed into the walls from the gas at any instant after an explosion. Hence, provided the heat liberated in the explosion was known, that remaining in the gas at any temperature, inferred from the pressure, could be estimated. The difficulty of accurately estimating the heat liberated by the burnt gas could not, however, for a long time be surmounted. It seemed that, when the coal-gas was mixed with air, there was a spontaneous time reaction between the two, which caused a discrepancy of something like 10 per cent in the volume of combustible gas, and a corresponding decrease in the actual amount of heat liberated at the time of the explosion. This difficulty was eventually overcome by mixing the combustible gas with either air or oxygen in a separate vessel some considerable time prior to charging the calorimeter.

The apparatus and calorimeter used by the author had many improvements over the original one described by Prof. Hopkinson, and, instead of using coal-gas of variable quality, and requiring extensive analysis and calorimetry, the less complex gases, hydrogen and carbon monoxide, were used, mixed with either air or oxygen.

At the time the experiments, the results of which are to be given, were initiated and carried out, the information available on the specific heats at high temperatures was obtained from the researches of Holborn and Austin, Holborn and Henning, Mallard and Le Châtelier, Langen and Clerk. Pier had published his results uncorrected, but Bjerram's corrections to Pier's results had not arrived. The Committee on Gaseous Explosions, appointed by the British Association, have fully considered the results of the former

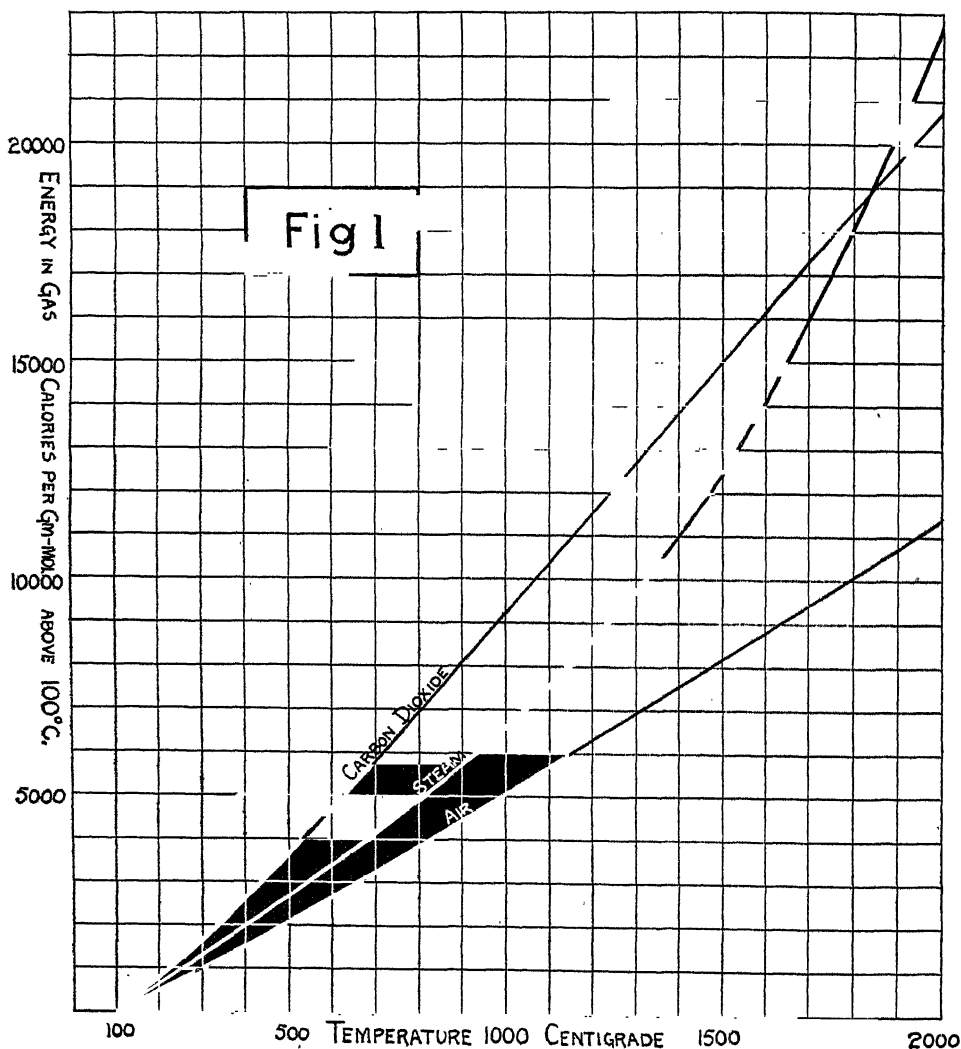
\* 'Roy. Soc. Proc.,' A, vol. 79 (1907).

workers, and their conclusions are contained in the various reports issued. Several different methods of research have been used, but there is no great uniformity in the results obtained by the various workers.

The explosion method of determining specific heats has several disadvantages, the chief of which are:—

(1) At the time of maximum pressure, chemical and thermal equilibrium by no means exist in the hot gases. That is, the whole of the heat has not been liberated, and the temperature across the mass of gas is not uniform.

(2) Since the calorimeter must have a certain number of small passages leading to and from it, for filling, indicating, sampling, etc., it follows that,



when the charge is exploded, a certain proportion of the gas is compressed into these spaces and does not burn. And thus it requires very careful gas analysis, both before and after the explosion, in order to make certain of the actual quantity of heat liberated.

The recording calorimeter allows the heat in the gas to be estimated at times considerably remote from that of maximum pressure, so that the chemical and thermal equilibrium will be more nearly attained.

The author's experiments were carried out with due regard to all the points mentioned. Analyses of the combustible mixture were made on samples from the mixing vessel before passing to the calorimeter, from the calorimeter before explosion, and from the calorimeter after explosion, and any experiment was rejected in which the gas quantities did not agree in all three of these analyses. About one hundred experiments of the present series were carried out, of which about half were with hydrogen and air, and the remaining quarters with carbon monoxide and air, and carbon monoxide and oxygen, respectively. In the calculations were finally used twenty-four of the hydrogen series, sixteen of the carbon monoxide and air, and twelve of the carbon monoxide and oxygen.

The results are shown in the curves of fig. 1, in which are plotted the heat contents above  $100^{\circ}\text{C}$ . of steam, air and carbon dioxide per gramme-molecule for temperatures ranging up to  $2000^{\circ}\text{C}$ . The actual range of the experiments is from  $1000^{\circ}$  to  $2000^{\circ}\text{C}$ ., and the lower parts have been filled in from the researches of Swann and Holborn and Henning. The figures from which the curves are prepared are given in Table I, together with the values of the mean volumetric heats for temperature gaps of  $100^{\circ}\text{C}$ . The hydrogen experiments gave the figures for steam and air, and the accuracy is believed to be within 1 or 2 per cent. The carbon dioxide curves are deduced as the phenomenon of after-burning was encountered, and so may be open to criticism.

#### *General Calculations.*

The quantities of heat liberated in the combustion of hydrogen to steam, and carbon monoxide to carbon dioxide, have been taken from Ostwald's '*Lehrbuch der Allgemeinen Chemie*,' vol. 2, and are based on the results of Andrews and Favre and Silbermann. The figures are as under:—

Hydrogen to steam—67,840 calories per gramme-molecule. Carbon monoxide to carbon dioxide—67,200 calories per gramme-molecule.

The hydrogen was purchased from the British Oxygen Company. The carbon monoxide was prepared by the author, 20 litres at a time, from sulphuric and oxalic acids, the carbon dioxide formed being absorbed by caustic soda.



Table I.—Energy in Gases per Gramme-Molecule above 100° C., and Mean Volumetric Heat per Gramme-Molecule from 0° C. to *t*° C. calories.

Temperature.	Air.		Steam.		Carbon dioxide.	
	Energy.	Mean volumetric heat.	Energy.	Mean volumetric heat.	Energy.	Mean volumetric heat.
° C.						
100	0	4·900	0	6·59	0	7·0
200	510	5·000	660	6·61	800	7·5
300	1,040	5·090	1,330	6·65	1,680	7·95
400	1,570	5·177	2,020	6·70	2,640	8·35
500	2,140	5·258	2,710	6·76	3,660	8·72
600	2,710	5·332	3,430	6·85	4,710	9·03
700	3,290	5·402	4,180	6·92	5,810	9·31
800	3,890	5·471	4,950	7·02	6,950	9·56
900	4,490	5·532	5,770	7·14	8,090	9·76
1,000	5,100	5·590	6,630	7·29	9,240	9·94
1,100	5,720	5·644	7,590	7·50	10,390	10·09
1,200	6,340	5·698	8,640	7·75	11,570	10·21
1,300	6,960	5·729	9,770	8·03	12,710	10·32
1,400	7,590	5·766	11,030	8·35	13,890	10·41
1,500	8,220	5·803	12,440	8·74	15,050	10·50
1,600	8,850	5·838	14,120	9·23	16,210	10·57
1,700	9,490	5·869	16,060	9·82	17,390	10·62
1,800	10,120	5·900	18,150	10·46	18,490	10·66
1,900	10,780	5·930	20,350	11·07	19,630	10·70
2,000	11,430	5·961	22,720	11·69	20,740	10·72

The quantity of gas burnt in an explosion was obtained from an analysis of the contents of the calorimeter after the explosion, together with the reduction of pressure caused by the chemical contraction, and, in the hydrogen experiments, the condensation of the steam. Analysis was also made of the mixture before admission to the calorimeter, and of the mixture actually in the calorimeter before explosion. These analyses all agreed. Hempel's pipettes and burettes were used for all the gases except hydrogen. The hydrogen was absorbed in a palladium tube.

The temperature of the gas at any instant was obtained from the pressure record given by a Watson type diaphragm indicator and calculated according to the usual gas laws:—

$$T_2 - T_1 = T_1 \left( \frac{p_2}{p_1^e} - 1 \right)$$

where  $T_1$  is the initial absolute temperature at pressure  $p_1$ ,

$T_2$  is the absolute temperature at pressure  $p_2$ ,

$e$  is the coefficient of chemical contraction in the gas reaction and is proportional to the volume of gas burnt;

for example: if 16 per cent. of either hydrogen or carbon monoxide are consumed

$$e = 1 - \frac{0.16}{2} = 0.92.$$

Thus, by suitable calibration of the indicator, the mean temperature of the gas may be measured directly from the photographic film.

The galvanometer, measuring the change of resistance of the copper coil, was calibrated on each film by marking the deflection due to a known change in the resistance of the coil arm of the bridge. This calibration made unnecessary the measurement of either the main current or of the other resistances in the bridge. For the very small deflection of the galvanometer encountered, the deflection is proportional to the change in resistance of the coil.

Of the heat which passes into the coil, a certain amount is conducted through to the backing between the coil and the cast-iron walls of the vessel. This has been taken into account by the method given by Hopkinson in his paper on "Radiation in a Gaseous Explosion,"\* in which the backing is assumed to be an infinite solid whose surface undergoes a definite change of temperature, and so the following relation is obtained:—

$$\frac{\text{Heat to backing at time } T}{\text{Heat to coil}} = \frac{2}{C} \sqrt{\left(\frac{kc}{\pi}\right)} \cdot \frac{1}{\theta_r} \int_0^T \frac{d\theta}{dt} \sqrt{[T-t]} \cdot dt,$$

where  $k$  and  $c$  are the thermal conductivity and capacity respectively per unit volume of the backing,  $C$  is a constant,  $\theta_r$  is the temperature of the coil at time  $T$ .

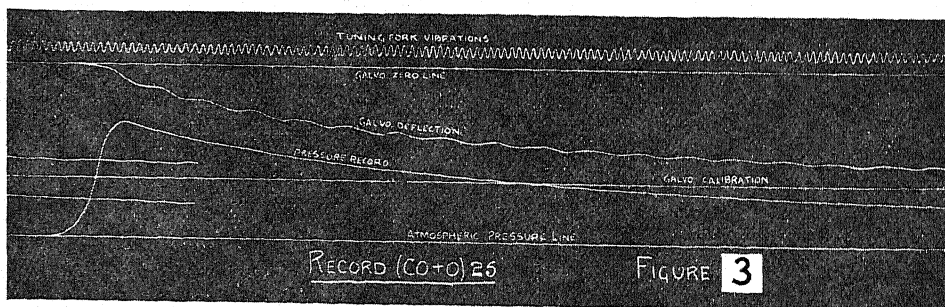
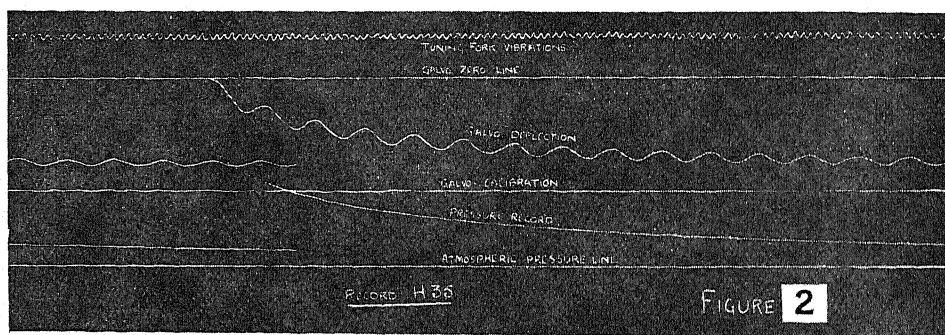
The temperature of the surface of the backing is assumed to be the mean temperature of the coil and is obtained from the galvanometer deflection. In order to find the constants, a balance of the heats is obtained at 1 second after ignition, and the heat unaccounted for is assumed to have passed through to the backing. The heat in the gas at 1 second in the case of the hydrogen experiments is taken from Holborn and Henning's results, as the temperature is in the neighbourhood of 500° C. From this the combined constant  $\frac{2}{C} \sqrt{\left(\frac{kc}{\pi}\right)}$  is obtained and the absolute value of the factors is not measured. The heat which has passed to the backing at 1 second, calculated in this manner, is never more than 9 per cent. of the heat lost at that time by the gas, and contains the combined errors of all the measurements throughout the experiment.

\* 'Roy. Soc. Proc.,' A, vol. 84 (1910).

In the case of the hydrogen experiments a mean of the values obtained for  $\frac{2}{C} \sqrt{\left(\frac{kc}{\pi}\right)}$  has been calculated and then used for the heat passed to the backing at any time in each experiment. A very considerable error in this heat is only a small proportion of the total heat loss, so that strict accuracy in this point is not very important. The mean value of the constant for the hydrogen experiments was found to be 0.0625. This value has had to be used in the carbon monoxide experiments for reasons to be given later.

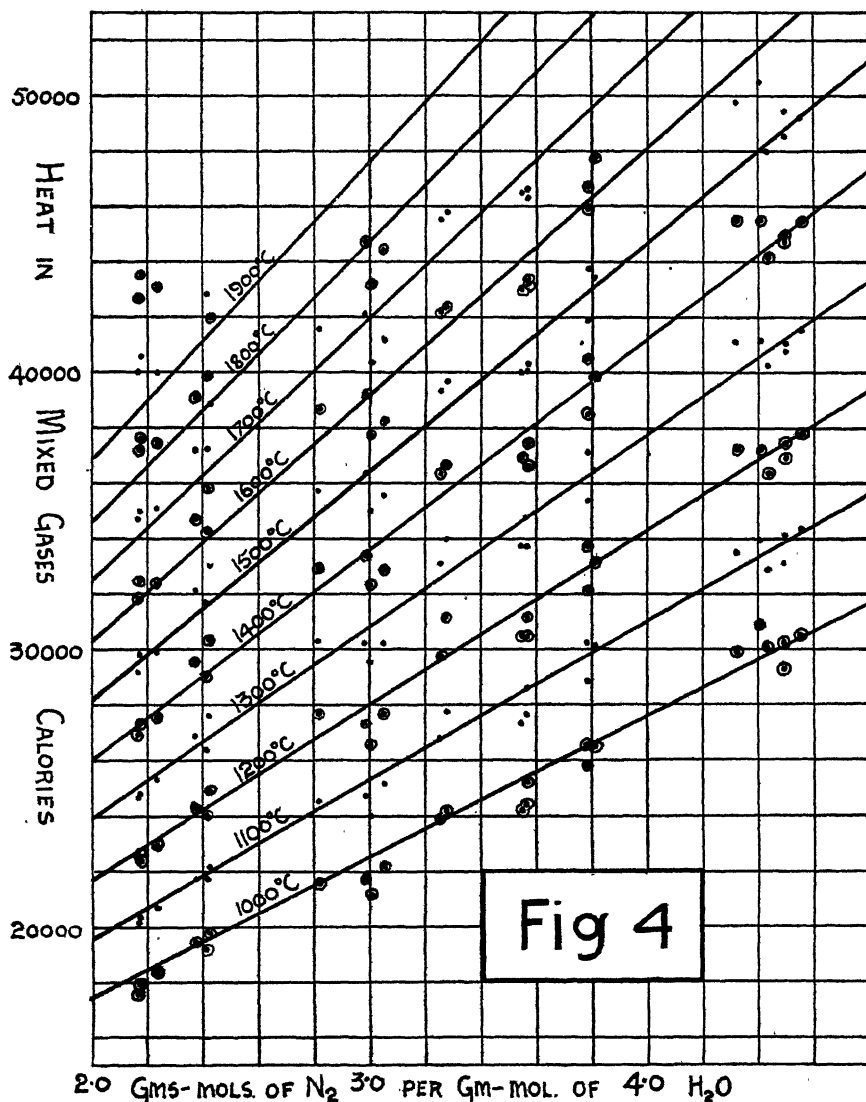
The calorimeter was 12 inches internal diameter by 12 inches long. The teak backing was  $\frac{1}{2}$  inch thick. The coil consisted of copper strip of  $\frac{1}{4}$  inch by  $1/16$  inch section, weighing with the fixing screws 4171 grms. The specific heat of the copper was 0.093 and the resistance temperature coefficient 0.00428. The resistance of the coil at 0° C. was 0.1202 ohms. The internal volume of the calorimeter was 18.5 litres and the internal area of surface 3935 sq. cm. The galvanometer calibrating resistance was 0.0148 ohms. The indicator gave a deflection of 1.31 inches for a rise in pressure of 100 lbs. per square inch.

Two representative films are given; fig. 2 for the hydrogen and fig. 3 for the carbon monoxide experiments.



*Hydrogen-Air Experiments.*

The heat liberated in the explosion is obtained from the amount of hydrogen estimated by the analyses as having been burnt. From the photographic record the heat which has passed into the walls at any temperature, suitably increased by the heat which has gone to the backing, is obtained. Thus the difference between these two quantities of heat is that remaining in the gas at the associated temperature. This remaining quantity is reduced to calories per gramme-molecule of gas cooling, and in order to bring the various gases



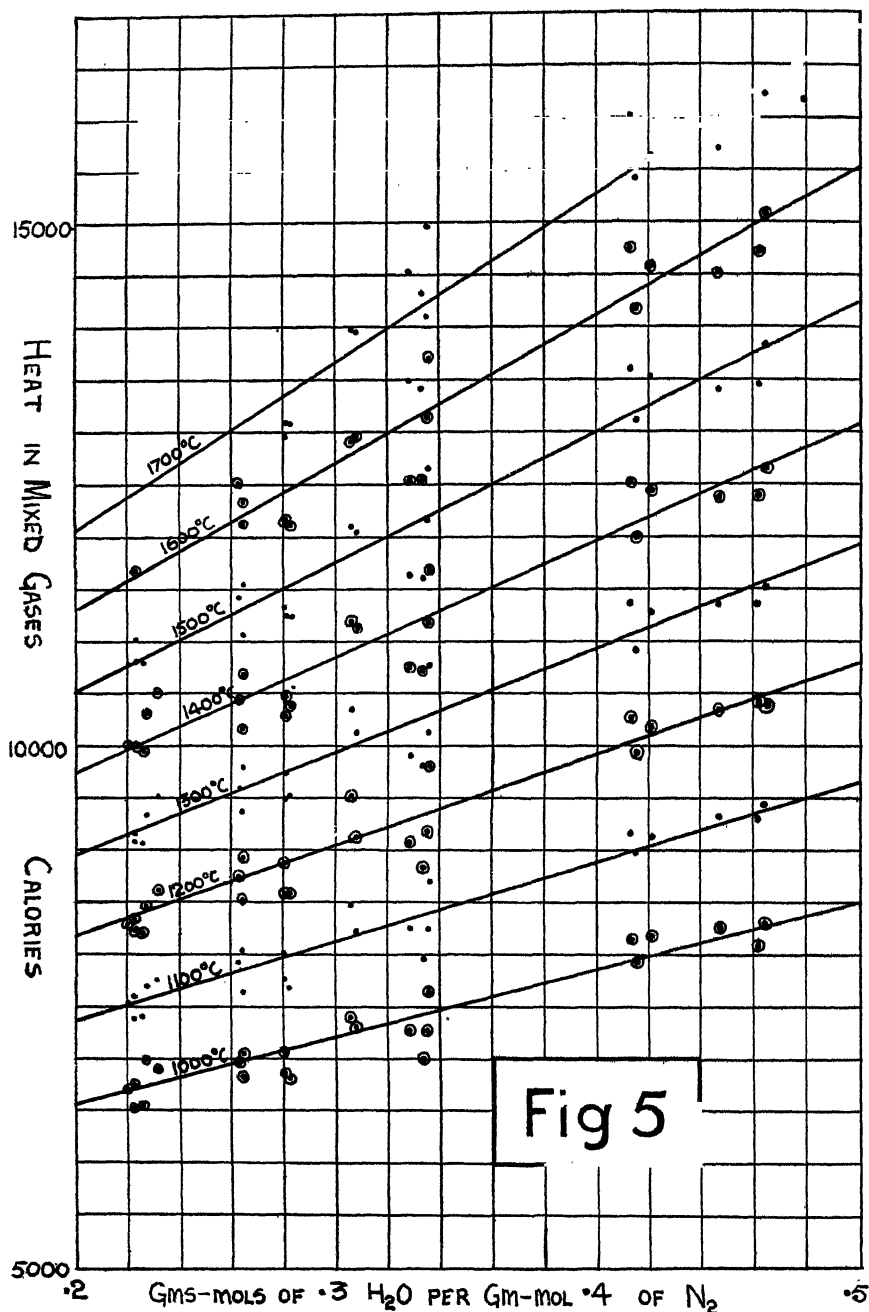
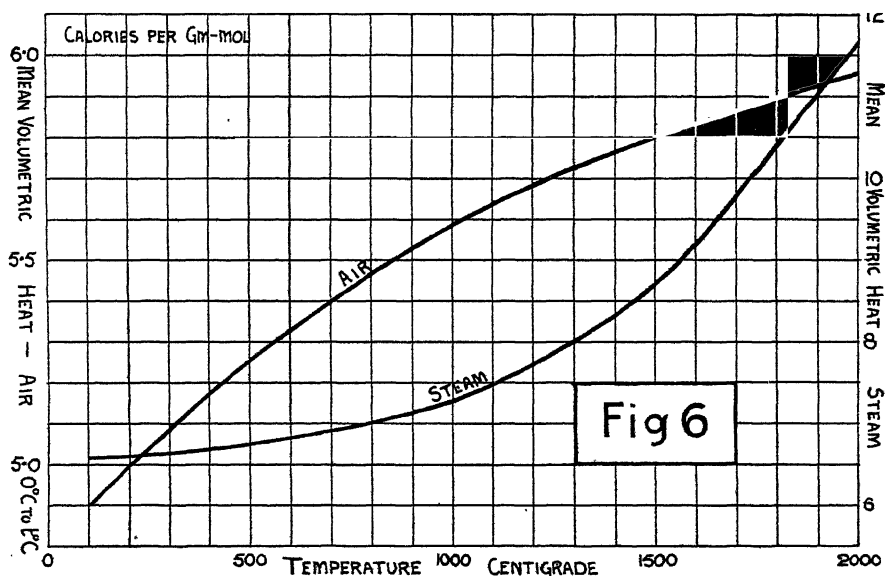


Fig 5

to the same basis for comparison, the heat necessary to raise the various constituents from the initial temperature of the experiment to  $100^\circ \text{C}$ . and convert the water to steam has been subtracted. Thus there is left the

amount of heat necessary to raise a gramme-molecule of gas, consisting of various proportions of steam and nitrogen, from  $100^{\circ}\text{C}.$  to temperatures ranging from  $1000^{\circ}\text{C}.$  to  $2000^{\circ}\text{C}.$  In order to allocate these quantities of heat, part to the steam and part to the nitrogen, it is necessary to adjust the volume of first the one and then the other of the constituents to an uniform amount throughout the series of experiments, and calculate the quantities of heat then contained by the mixture accordingly. This procedure gives two sets of heat contents. In the one the volume of steam is constant and the nitrogen varies, and in the other the volume of nitrogen is constant and the steam varies. Curves can then be drawn showing the relation between the volume of the variable constituent and the heat contents of the mixture at various temperatures. These curves are shown in figs. 4 and 5. The points obtained are seen to lie sensibly on series of straight lines for the various temperatures, and the slopes of the lines give the heat contents of the variable constituent for the appropriate temperature. The mean positions of the lines through the points were obtained in a mechanical manner in order to avoid the personal element.

The values of the mean volumetric heat between  $1000^{\circ}\text{C}.$  and  $2000^{\circ}\text{C}.$  were then calculated, and completed between  $100^{\circ}\text{C}.$  and  $1000^{\circ}\text{C}.$  from the



researches of other workers. These curves are given for steam and nitrogen in fig. 6.

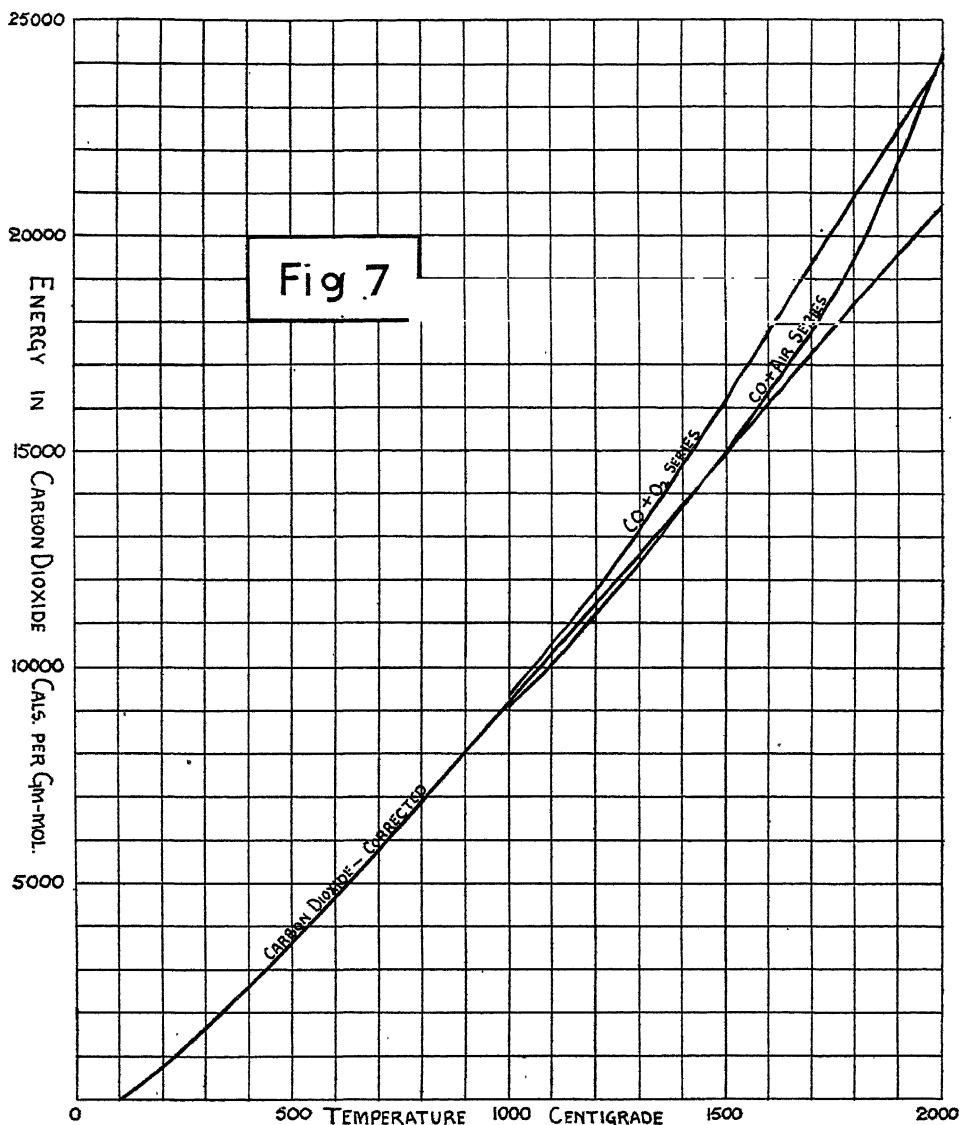
*Carbon Monoxide Experiments.*

In this series the temperature at one second was about 950° C. As a first approximation Holborn and Henning's values for the heat in the gas at one second were used, and it was found that there was a very considerable balance of heat to be accounted for as having passed through to the backing; in fact, much more than could possibly be the case, so the value of  $\frac{2}{C} \sqrt{\left(\frac{kc}{\pi}\right)}$  from the hydrogen experiments was used and an amount of heat left unaccounted for. This latter quantity was found to increase with the strength of mixture burnt. It was first thought that Holborn and Henning's values must be far too low, and hence the heat unaccounted for was assumed to be contained by the carbon dioxide. The heat in this gas was then deduced by using the heat in the air as obtained from the hydrogen experiments. It was found, however, that the heat in the carbon dioxide at any temperature showed a definite increase with the strength of mixture exploded, which would not seem actually to be possible.

Another explanation is, that combustion, even at 1 second after ignition, is still incomplete. The photographic records show much slower combustion with the carbon monoxide than with hydrogen. Also the galvanometer spot in the hydrogen experiments is in a state of vibration entirely absent with carbon monoxide, which seems to indicate actual flame contact with the walls in the case of hydrogen, whilst the carbon monoxide flame dies out some distance away. This will leave an unburnt gas layer near the walls, which may eventually burn as the pressure falls and allows the gas to expand into the open again.

The results for air and steam are about 7½ per cent. higher than those of Holborn and Henning at 800° C., and it is reasonable to assume that their values for carbon dioxide are a similar amount too low. This figure has therefore been taken, the values of the mean volumetric heat between 100° C. and 200° C. obtained from Swann's values, and a free curve drawn through the points and carried along to 1000° C. The heat in the carbon dioxide at 1 second has been deduced from this curve. The heat actually accounted for at 1 second has been taken as the heat actually liberated at that time. This heat is made up of that in the carbon dioxide and air, that in the coil and that passed through to the backing, calculated by using  $\frac{2}{C} \sqrt{\left(\frac{kc}{\pi}\right)}$  from the hydrogen experiments. The balance between the quantity of heat accounted for and that eventually liberated has been considered as still latent in the unburnt gas layer in contact with the walls. The heat accounted for at one second has been used to determine the heat left in the mixed gases at

times previous to 1 second. The heat in the air from the hydrogen experiments has been subtracted from this remainder, and thus the heat in the carbon dioxide should be left. The latter quantities are converted to calories per gramme-molecule above  $100^{\circ}\text{C}$ ., and the average of the two

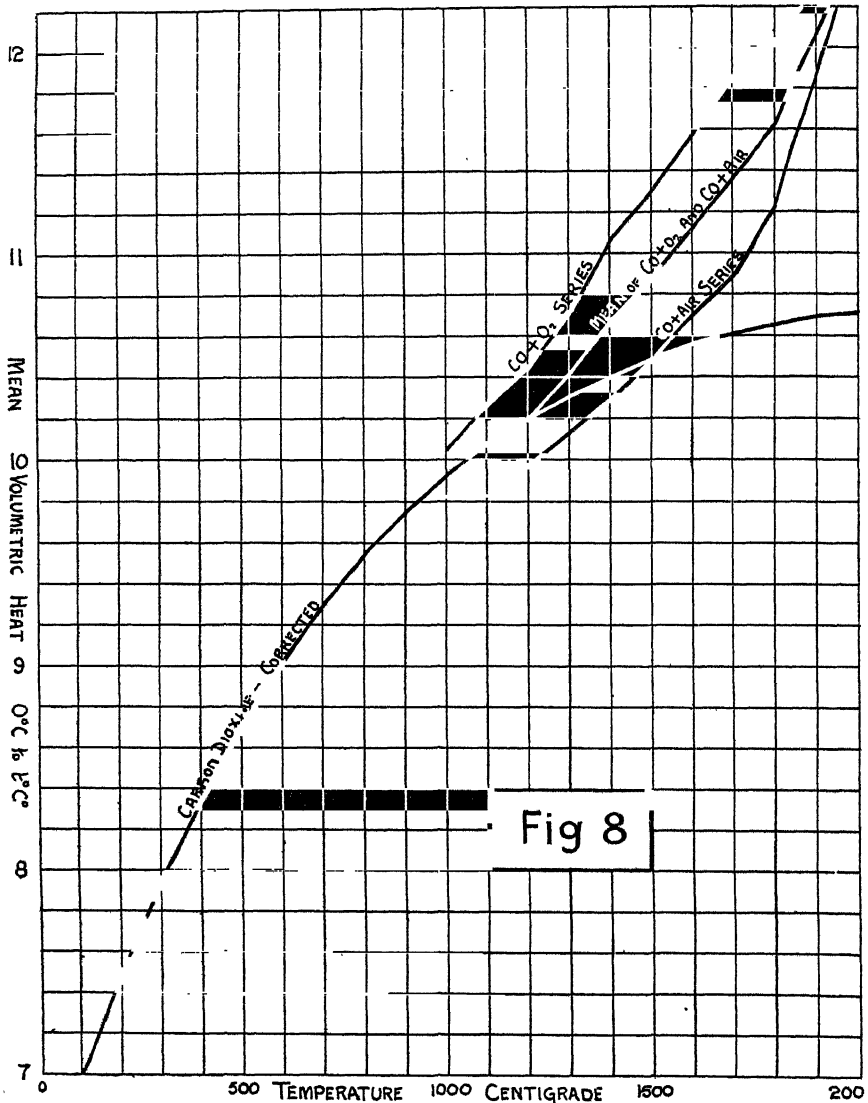


series, carbon monoxide and air and carbon monoxide and oxygen, are shown in fig. 7. The values of the mean volumetric heat are shown in fig. 8.

It is evident that if a certain amount of carbon monoxide is still unburnt at the expiration of one second, even more will be unburnt at times earlier



than this, and thus the amount of heat left in the carbon dioxide will be too large by an increasing amount, as the time from ignition is shorter. As there seems to be no method of estimating the amount of unburnt gas at any earlier period the volumetric heat curve has been continued in a free manner



up to 2000° C., and the heat actually in the carbon dioxide deduced from this. It will be noticed that the carbon monoxide—oxygen experiments give results somewhat higher than the carbon monoxide—air experiments. The variation is about 2 per cent. at 1000° C., 6 per cent. at 1500° C., and gradually

decreases to 1 per cent. at 2000° C. In the former experiments the products of combustion are carbon dioxide and oxygen, and in the latter, carbon dioxide and nitrogen. The difference represents a very small quantity of heat in the actual volume of carbon dioxide present after explosion and is possibly within the limits of error of the experiments. Otherwise a small difference in the heat contents of the oxygen and nitrogen would bring the curves together, if that in the oxygen were the larger. Up to 800° C., however, Holborn and Henning found the reverse to be the case. It was also noticed that there was a greater proportion of unburnt carbon monoxide in the oxygen experiments than in those with air, and the temperatures at one second are considerably lower.

A mean of the volumetric heats for the two curves has been obtained. This mean curve lies along the free curve up to 1200° C., and beyond this temperature rises above the free curve at an uniform rate to about 1700° C. Above 1700° C. the rate of separation of the curves makes a further increase. It is thought that the difference between the curves from 1200° to 1700° C. will solely represent an increasing amount of unburnt gas. At higher temperatures the difference will include any dissociation, and also the lack of thermal equilibrium, as the higher temperatures are very close to the point of maximum pressure.

It is clearly recognised that the whole of the figures for carbon dioxide are deduced, but it is thought that the basis is sufficiently sound, at least from 1000° to 1200° C., to warrant the acceptance of the results to within 2 per cent. Above 1200° C. the figures are obtained from a free curve which has no checking point at the higher temperature end, and so may be considerably in error. It is thought, however, that they are likely to be more correct than those of Langen, or of Mallard and Le Châtelier, which have been taken up to the present, as it would seem that their experiments also must contain this unburnt gas, for which no correction seems to have been made.

The author would like to dedicate this work to the late Prof. Bertram Hopkinson, as the idea of the calorimeter was his, and he first suggested the line of research to the author. The work represented in this paper was carried out, after the death of Prof. Hopkinson, in the Engineering Laboratories of Cambridge University, and the author would like to thank Prof. Inglis and Mr. C. G. Lamb for their kindness in placing the resources of the laboratories at his disposal.

## APPENDIX I.

*The Effect of the State of the Walls of the Containing Vessel on the Rate of Heat Flow in a Gaseous Explosion.*

Measurements on the radiation from the gas to the walls of the containing vessel under different conditions were made by Mr. W. T. David. They are described in his paper, "Radiation in a Gaseous Explosion."\* The author carried out a series of experiments with the Hopkinson calorimeter, to find the total heat passed to the walls after an explosion, first with the walls polished, and then blackened. The polished surface of the copper coil was obtained by the use of petrol, bath brick and rags, chiefly the latter, and rubbing was continued until no further change was visible to the naked eye. The other surface was obtained by painting over the coil with vegetable

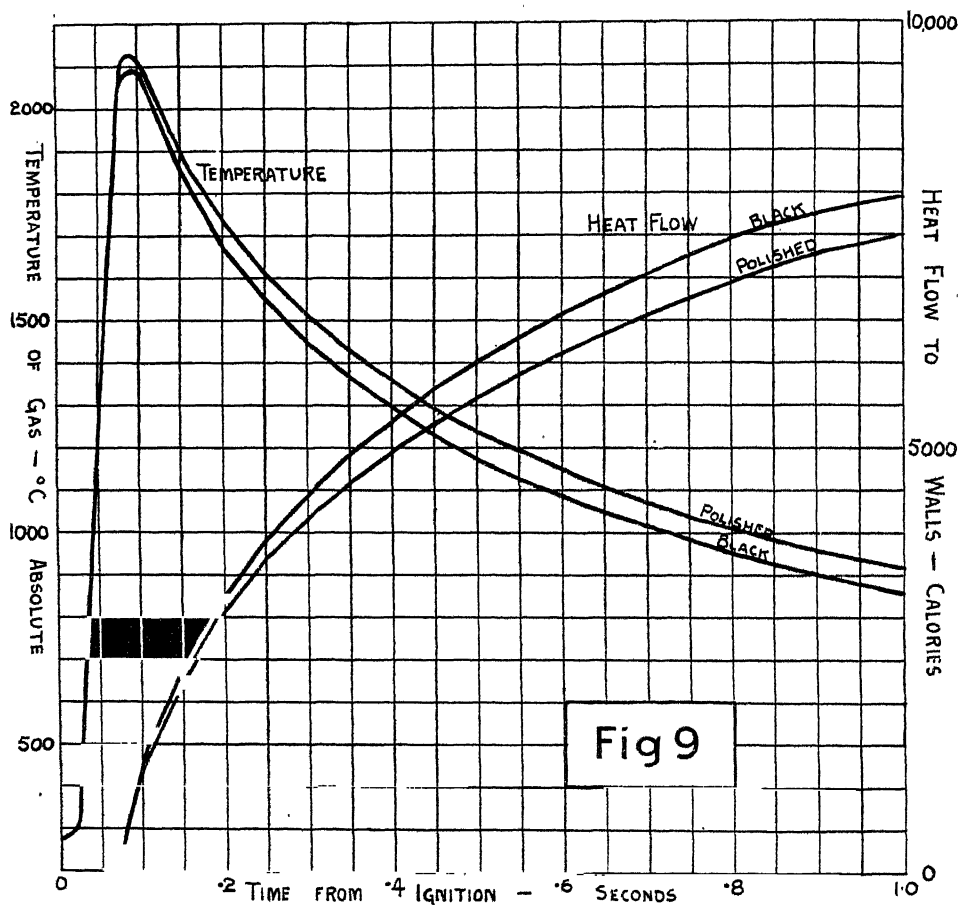
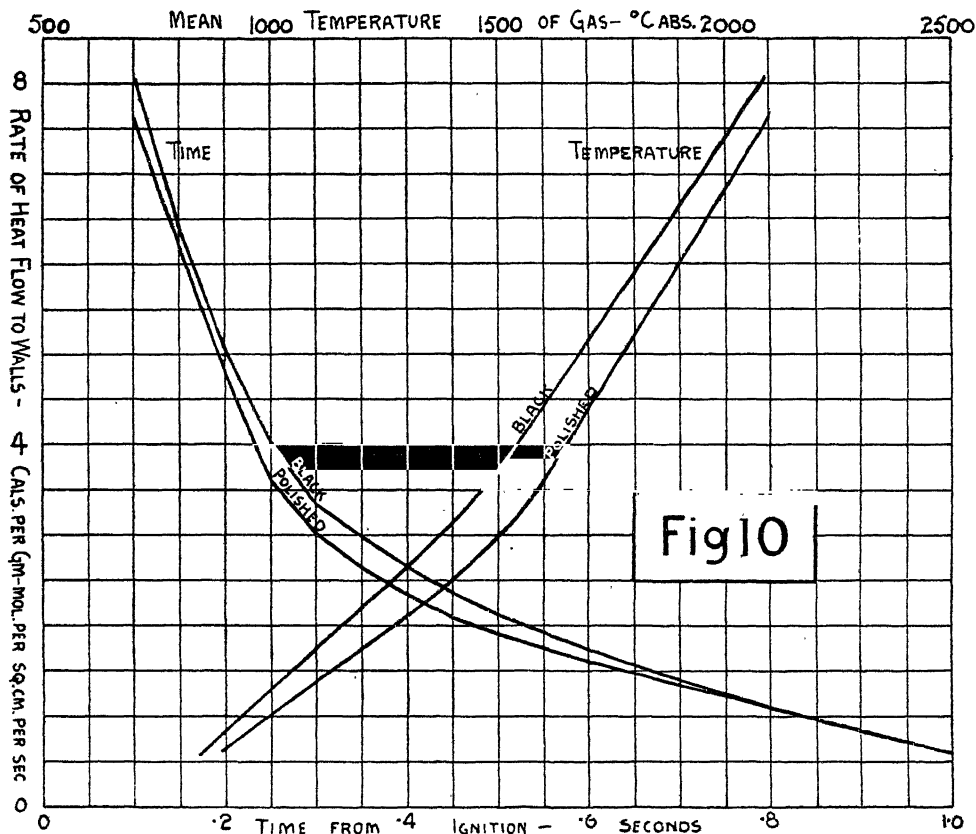


Fig 9

\* 'Roy. Soc. Proc.,' A, vol. 211 (1910).

black, the medium being petrol, and the walls were a dull black when dry. Coal gas was used in the combustible mixture, and five experiments, under each of the different conditions, were made. The same mixture strength was used throughout, viz., 12.35 per cent. of coal gas by volume.

The cooling curve and the total heat loss to the walls are shown in fig. 9. The maximum temperatures reached are  $2123^{\circ}$  and  $2089^{\circ}$  C. absolute respectively, giving a difference of  $34^{\circ}$  C. At the end of 1 second the gases have



cooled to  $918^{\circ}$  and  $859^{\circ}$  C. absolute, a difference at this point of  $59^{\circ}$  C. It may be noted that the heat lost to the walls in the two cases, when cooling has proceeded to the same temperature, is sensibly the same. To convert the heat lost to the walls to calories per square centimetre per gramme-molecule of gas cooling, the figures on the curve should be multiplied by the factor 0.000338.

At 1 second, the heat passed to the walls per square centimetre per gramme-molecule is 2.675 and 2.556 calories respectively.

David found that, at the end of 1 second, in a 13 per cent. mixture, the heat received in the walls by radiation was about 0.81 calories, with walls and bolometer black. This, taken in conjunction with the above figures, show that 30 per cent. of the heat lost by the gas at 1 second is radiated to the walls, and the remaining 70 per cent. passes by conduction, etc.

Fig. 10 shows the rate of heat flow to the walls at various times during the cooling, and it will be seen that during the first half second the rate is much greater with the walls black than when they are polished. After this time the rates seem to be practically the same in the two cases. The rate of heat flow at various temperatures is also shown in fig. 10, and indicates a 16 per cent. higher rate throughout with the blackened walls.

Plotted logarithmically, the temperature curves from fig. 10 give the following relations between the rate of heat flow and the difference of mean gas temperature and walls:—

$$\text{for black walls} \quad \frac{dH}{dt} = 1.766 \times 10^{-6} \times T^{2.054},$$

$$\text{for polished walls} \quad \frac{dH}{dt} = 1.462 \times 10^{-6} \times T^{2.059},$$

where  $T$  is the difference between the average temperature of the walls and the mean temperature of the gas,

$\frac{dH}{dt}$  is the rate of heat flow to the walls in calories per square centimetre per second per gramme-molecule of gas cooling.

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*The Effect of Shallow Water on Wave Resistance.*

By T. H. HAVELOCK, F.R.S.

(Received October 28, 1921.)

1. The general character of experimental results dealing with the effect of shallow water on ship resistance may be stated briefly as follows:—At low velocities the resistance in shallow water is greater than in deep water, the speed at which the excess is first appreciable varying with the type of vessel. As the speed increases, the excess resistance increases up to a maximum at a certain critical velocity, and then diminishes. With still further increase of speed, the resistance in shallow water ultimately becomes, and remains, less than that in deep water at the same speed. The maximum effect is the more pronounced the shallower the water. For further details and references one may refer to standard treatises, but one quotation may be made in regard to the critical velocity: "This maximum appears to be at about a speed such that a trochoidal wave travelling at this speed in water of the same depth is about  $1\frac{1}{4}$  times as long as the vessel. . . . It was at one time supposed that the speed for maximum increase in resistance was that of the wave of translation. This, however, holds only for water whose depth is less than 0.2 times the length of the vessel. For greater depths the speed of the wave of translation rapidly becomes greater than the speed of maximum increase of resistance."\* In a recent analysis of the data, H. M. Weitbrecht† expresses a similar conclusion by stating that for each depth of water there is a critical velocity, but that the critical velocity does not vary as the square root of the corresponding depth.

It should be noted that experimental results are for the total resistance. If we assume that this can be separated into three terms, which are simply additive, namely, eddy, frictional, and wave-making resistance, it must be admitted that probably all are affected by limited depth of water. However, the main differences are due to the altered wave-making, and the general explanation is to be found in the fact that there is a limiting velocity,  $\sqrt{gh}$ , for simple straight-crested waves on water of depth  $h$ .

Leaving aside the difficult problem of a solid body towed or driven through the water, we may study the allied problem of a given distribution of surface pressure and the associated wave resistance. Previous calculations of wave resistance have been limited to a line distribution of pressure, involving

\* D. W. Taylor, 'Speed and Power of Ships,' p. 114; also G. S. Baker, 'Ship Form, Resistance and Screw Propulsion,' p. 134.

† H. M. Weitbrecht, 'Jahrbuch d. Schiffbautech. Gesell,' vol. 22, p. 122 (1921).

therefore, only straight-crested parallel waves and so emphasising the connection between the critical velocity and that of the wave of translation. In the present paper I obtain an expression for the wave resistance of a surface pressure symmetrical about a point, and moving over water of finite depth. The result is in the form of a definite integral, which has been evaluated by numerical and graphical methods so as to give graphs of the variation of wave resistance with speed for different values of the ratio of the depth of water to the length associated with the pressure distribution. The graphs are of special interest in the cases intermediate between the two extremes of deep water and shallow water. They show the double effect of limited depth, in lowering the normal wave-making speed of the ship and in increasing the magnitude of the effect as the speed approaches that of the wave of translation. The results are discussed in their bearing upon the experimental results which have just been described.

2. In a previous paper\* I worked out the case of a symmetrical surface pressure moving over deep water. The present analysis is on exactly similar lines, except for suitable changes in the expressions; it may be sufficient, therefore, to set forth the calculation briefly, referring to the previous paper for further detail in the argument.

Take axes  $Ox, Oy$  in the undisturbed horizontal surface of water of depth  $h$  and  $Oz$  vertically upwards. For an initial impulse symmetrical about the origin, that is if the initial data are

$$\rho\phi_0 = F(\varpi), \quad \zeta = 0, \quad (1)$$

where  $\varpi^2 = x^2 + y^2$ , the velocity potential and surface elevation in the subsequent fluid motion are given by

$$\begin{aligned} \rho\phi &= \int_0^\infty f(\kappa) \cosh \kappa(z+h) \operatorname{sech} \kappa h J_0(\kappa\varpi) \cos(\kappa Vt) \kappa d\kappa, \\ g\rho\zeta &= - \int_0^\infty f(\kappa) J_0(\kappa\varpi) \sin(\kappa Vt) \kappa^2 V d\kappa, \end{aligned} \quad (2)$$

where

$$\begin{aligned} V^2 &= (g/\kappa) \tanh \kappa h, \\ f(\kappa) &= \int_0^\infty F(\alpha) J_0(\kappa\alpha) \alpha d\alpha. \end{aligned} \quad (3)$$

We obtain the effect of a travelling pressure system by integrating with respect to the time. We shall suppose that the system has been moving for a long time with uniform velocity,  $c$ , in the direction of  $Ox$ . Transferring to a moving origin at the centre of the system, we replace  $x$  in (2) by  $x+ct$ , and we find for the surface elevation

$$g\rho\zeta = - \int_0^\infty e^{-1/2\mu t} dt \int_0^\infty f(\kappa) J_0[\kappa\{(x+ct)^2 + y^2\}^{1/2}] \sin(\kappa Vt) \kappa^2 V d\kappa, \quad (4)$$

\* 'Roy. Soc. Proc.,' A, vol. 95, p. 354 (1918).

where  $f(\kappa)$  is found from the assigned pressure distribution,  $p = F(\varpi)$ , by means of (3). The factor  $\exp. (-\frac{1}{2}\mu t)$  serves to keep the integrals determinate, so that they give a solution which corresponds to the main part of the surface waves trailing aft from the moving disturbance. It is to be noted that ultimately  $\mu$  is made zero in the final results, and it is only retained in the intermediate analysis to a degree sufficient to attain its chief purpose. It should be stated also that all the analysis is subject to the usual limitation that the slope of the surface is supposed to be always small.

We take the wave resistance to be the resolved part of the pressure system in the direction of motion, or

$$R = \int F(\varpi) \frac{\partial \zeta}{\partial x} dS, \quad (5)$$

taken over the whole surface.

The disturbance (4) may be analysed into plane waves ranged at all possible angles to  $Ox$ . Substituting

$$\pi J_0 [\kappa \{ (x+ct)^2 + y^2 \}^{1/2}] = \int_0^\pi e^{i\kappa(x+ct)\cos\phi} \cos(\kappa y \sin\phi) d\phi, \quad (6)$$

we can integrate with respect to  $t$ , and obtain, after rejecting superfluous terms in  $\mu$ ,

$$\int_0^\infty e^{-1/2\mu t} e^{i\kappa ct \cos\phi} \sin(\kappa Vt) dt = -\frac{V \sec^2 \phi}{\kappa c^2 - g \sec^2 \phi \tanh \kappa h + i\mu c \sec \phi}. \quad (7)$$

Using this in (4), the surface elevation can be expressed in the form

$$2\pi\rho\zeta = \int_{-\pi/2}^{\pi/2} \sec^2 \phi d\phi \int_0^\infty \kappa f(\kappa) \tanh \kappa h \left\{ \frac{e^{i\kappa(x \cos \phi + y \sin \phi)}}{\kappa c^2 - g \sec^2 \phi \tanh \kappa h + i\mu c \sec \phi} + \frac{e^{-i\kappa(x \cos \phi + y \sin \phi)}}{\kappa c^2 - g \sec^2 \phi \tanh \kappa h - i\mu c \sec \phi} \right\} d\kappa. \quad (8)$$

3. We simplify the calculations by specifying the surface distribution of pressure as

$$p = F(\varpi) = Al/(l^2 + \varpi^2)^{3/2}, \quad (9)$$

where  $A$  and  $l$  are constants. It follows from (3) that  $f(\kappa) = Ae^{-\kappa l}$ . Now in (8) consider an element making an angle  $\phi$  with the axis  $Ox$ . Change to axes  $Ox'$ ,  $Oy'$ , given by  $x' = x \cos \phi + y \sin \phi$ ,  $y' = y \cos \phi - x \sin \phi$ . Then the integral with respect to  $\kappa$  becomes

$$\int_0^\infty \kappa e^{-\kappa l} \tanh \kappa h \left\{ \frac{e^{i\kappa x'}}{\kappa c^2 - g \sec^2 \phi \tanh \kappa h + i\mu c \sec \phi} + \frac{e^{-i\kappa x'}}{\kappa c^2 - g \sec^2 \phi \tanh \kappa h - i\mu c \sec \phi} \right\} d\kappa. \quad (10)$$



As in similar plane wave problems, this integral can be modified by integrating round a suitable contour in the plane of a complex variable; the expressions then divide into two types according as the integrand has or has not a pole within the contour. The surface disturbance corresponding to (10) is seen then to consist, in general, of a surface elevation symmetrical with respect to the line  $x \cos \phi + y \sin \phi = 0$ , together with a regular train of waves in the rear of this line; but the latter part only occurs if  $c^2 \cos^2 \phi < gh$ . In evaluating the wave resistance by (5) for the symmetrical distribution (9), we see that we need only consider the regular train of waves. By calculating the residue of the integrand in (10), collecting the results and finally making  $\mu$  zero, we find that the regular waves, when they occur, are given by

$$\frac{4\pi A c^2 \kappa^2 e^{-\kappa l} \sin(\kappa x')}{g \sec^2 \phi (c^2 - gh \sec^2 \phi) + \kappa^2 c^4 h}, \quad (11)$$

where  $\kappa$  is the root of

$$\kappa c^2 - g \sec^2 \phi \tanh \kappa h = 0; \quad gh \sec^2 \phi > c^2. \quad (12)$$

From (5) and (11), the contribution of this element to the wave resistance is

$$\begin{aligned} \frac{4\pi A c^2 \kappa^3 e^{-\kappa l} \cos \phi}{g \sec^2 \phi (c^2 - gh \sec^2 \phi) + \kappa^2 c^4 h} \int_{-\infty}^{\infty} dy' \int_{-\infty}^0 \frac{\Delta l \cos(\kappa x')}{(x'^2 + y'^2 + l^2)^{3/2}} dx' \\ = \frac{4\pi^2 A^2 c^2 \kappa^3 e^{-2\kappa l} \cos \phi}{g \sec^2 \phi (c^2 - gh \sec^2 \phi) + \kappa^2 c^4 h}. \end{aligned} \quad (13)$$

Summing for the different elements, from (13) and (7), we have finally for the wave resistance

$$R = \frac{4\pi A^2 c^2}{\rho} \int_{\phi_0}^{\pi/2} \frac{\kappa^3 e^{-2\kappa l} \sec \phi d\phi}{g \sec^2 \phi (c^2 - gh \sec^2 \phi) + \kappa^2 c^4 h}, \quad (14)$$

where  $\kappa$  satisfies  $\kappa c^2 = g \sec^2 \phi \tanh \kappa h$ , and the lower limit  $\phi_0$  is given by

$$\phi_0 = 0, \text{ for } c^2 < gh; \quad \phi_0 = \arccos (gh/c^2)^{1/2}, \text{ for } c^2 > gh. \quad (15)$$

4. We may notice, in the first place, that (14) reduces to the expression given previously for deep water; making  $h \rightarrow \infty$ , we find

$$\begin{aligned} R &= (4\pi g^2 A^2 / \rho c^6) \int_0^{\pi/2} \sec^5 \phi e^{-2(g l / c^2) \sec^2 \phi} d\phi \\ &= \frac{\pi^2 A^2 x^3 e^{-x}}{2g \rho l^3} \left\{ i H_0^{(1)}(ix) - \frac{1+2x}{2x} H_1^{(1)}(ix) \right\}, \end{aligned} \quad (16)$$

where  $x = gl/c^2$ , and the result is expressed in terms of Bessel functions of which Tables are available. For finite values of the ratio  $h/l$ , the value of  $R$  for given values of  $c$  can only be obtained from (14) by numerical and graphical methods. After some preliminary trial, the following plan was

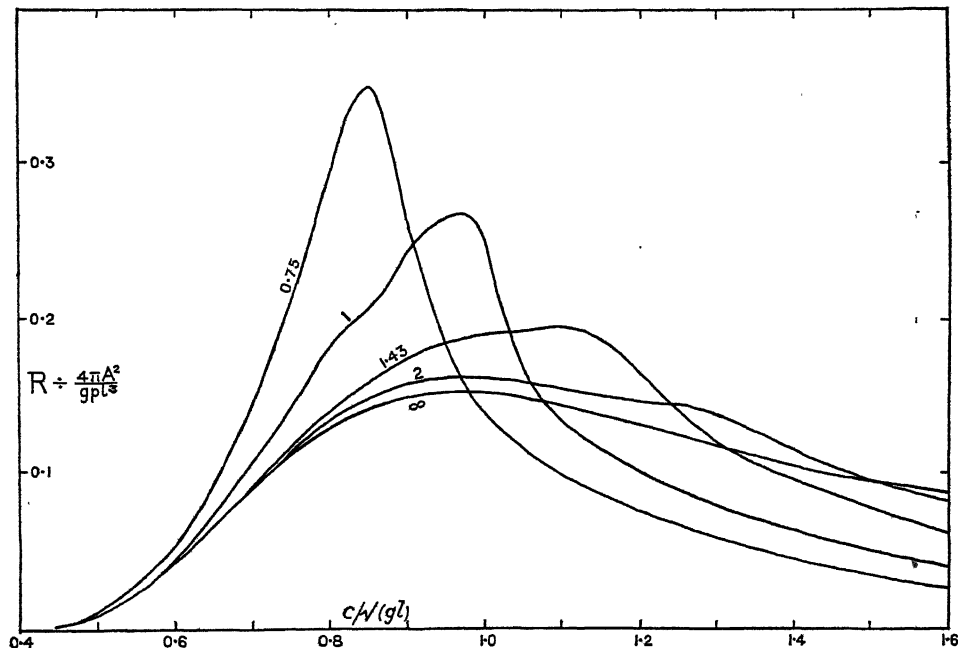
adopted. With  $p = h/l$ , and  $\alpha = \kappa h$ , using the relation between  $\kappa$  and  $\phi$ , (14) can be put in the form

$$R = \frac{4\pi A^2 x^{1/2}}{g\rho l^3 p^{5/2}} \int_{\phi_0}^{\pi/2} \frac{\alpha^{7/2} e^{-2\alpha/p} \coth^{1/2} \alpha}{\alpha^2 + \alpha \coth \alpha - \alpha^2 \coth^2 \alpha} d\phi, \quad (17)$$

with  $\alpha \coth \alpha = px \sec^2 \phi. \quad (18)$

For a given value of  $p$ , the integrand of (17), which we may denote by  $f(\alpha)$ , was calculated for values of  $\alpha$  ranging from zero to 3 at intervals of 0.2, and in certain cases also at unit intervals up to the value 10. Taking next an assigned value of  $x$ , the value of  $\phi$  corresponding to each value of  $\alpha$  was found from (18). The integrand  $f(\alpha)$  was then graphed on a base of  $\phi$ , giving a curve for each value of  $x$ ; the area of the curve was taken by an Amsler radial planimeter, and then the value of (17) was obtained. The calculations are rather lengthy and it is unnecessary to repeat them here.

The process was carried out for  $p = 2, 1.43, 1, 0.75$ , with about a dozen values of  $x$  in each case; some estimates were also made for  $p = 0.5$ , to confirm the general deductions. Further, the values for  $p = \infty$  were calculated from (16). The results are shown in the figure, where the unit for  $R$  is  $4\pi A^2/g\rho l^3$ , and for  $c$  is  $\sqrt{gl}$ .



5. The curve for deep water,  $p = \infty$ , has a single maximum at a velocity slightly less than  $\sqrt{gl}$ . At this velocity the corresponding length of

simple transverse waves is about  $2\pi l$ ; this may be called the principal wave-making length of the disturbance, to use a term from the theory of ship resistance. Taking next the curve for  $p = 2$ , we can see indications of two maxima. The first occurs at about the point 0.97 on the velocity scale; it clearly corresponds to the deep water maximum, and comes lower down the scale, because waves of given length occur at a lower velocity as the depth diminishes. There is also a second maximum at a velocity of about 1.25; this is due to the other factor in the resistance, namely, the increased effect as the velocity approaches the velocity  $\sqrt{gh}$  of the so-called wave of translation, which in this case is at the point 1.41 on the velocity scale.

From the next curves,  $p = 1.43$  and  $p = 1$ , we see the increasing importance of the latter effect as the depth becomes less. For the curve  $p = 1.43$ , there is a maximum near the velocity 1.1, the corresponding value of  $\sqrt{gh}$  on the scale being 1.2. There is no other actual maximum, but there is an enhanced resistance at about 0.92, followed by a flattening of the curve between that point and the point 1.05; we may take the increased effect at 0.92 to correspond to the deep water maximum in the lower curves. Similarly for the curve  $p = 1$ , the corresponding values are: increased effect at about 0.81, diminished slope of curve between 0.82 and 0.9, maximum at 0.97, velocity of wave of translation 1.0. The last curve,  $p = 0.75$ , shows that, as the depth becomes small, the second effect becomes the predominant feature; the excess resistance increases rapidly in magnitude, and occurs practically at the velocity  $\sqrt{gh}$ . This effect is still more pronounced for  $p = 0.5$ , but the results are not shown in the figure. It is obvious that, as the ratio of  $h/l$  diminishes, the disturbance becomes more like that due to a line disturbance; in simple calculations on the latter assumption, the resistance increases indefinitely at the velocity  $\sqrt{gh}$ , and falls suddenly to zero above that velocity. It will be seen from the figure that in all cases the resistance falls after the velocity  $\sqrt{gh}$ , as, in fact, may be deduced directly from the expression (17).

In a comparison between these results and the experimental curves of ship resistance described in § 1, it is advisable to consider in each case the difference between the resistance in water of a given depth and that in deep water; in this sense the results agree in character. Thus the first effect of finite depth may be regarded as due to the lowering of the chief wave-making velocity; it is only when the depth of water becomes of the same order as the beam of the ship that the critical velocity is practically that of the wave of translation.

In describing the experimental curves, it was stated that the excess resistance has a maximum value at a certain critical velocity. But there is

one exceptional set of curves, obtained at the United States Model Basin,\* which shows two maxima: a phenomenon which has not received explanation. It is conceivable that this may be a case in which the two maxima indicated in the intermediate curves of the present paper have become prominent through some unusual features of the model. In this connection, it must be remembered that the present calculations are based upon a surface pressure of specially simple type, one symmetrical round a point; one could extend the calculations by integration, as in the previous results for deep water, so as to apply to a pressure distribution, giving a better analogy with ship form. It may be anticipated that the results would be of the same character in general, though no doubt better agreement could be obtained in certain details.

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*The Diffraction of Plane Electromagnetic Waves by a Perfectly Reflecting Sphere.*

By F. PURYER WHITE, M.A., Fellow of St. John's College, Cambridge.

(Communicated by Dr. T. J. I'A. Bromwich, F.R.S. Received June 9, 1921.)

*Introduction.*—The problem of the diffraction of electromagnetic waves by a perfectly conducting sphere is of interest both from the point of view of wireless and from that of physical optics. Two cases may be considered: (1) when the source of the waves is a Hertzian oscillator on the surface of the sphere; and (2) when the waves are plane. The formal series solution of both these problems has been given by several writers, including Sir J. J. Thomson, the late Lord Rayleigh, and Prof. H. M. Macdonald. For a sphere of which the radius is small compared with the wave-length the series converge rapidly and are suitable for computation, but for a large sphere the important terms are far on in the series and the latter must be transformed in order to get formulæ which may be of use.

For case (1) this problem has been attacked by Macdonald, Poincaré, J. W. Nicholson, A. E. H. Love and several others, but case (2) has not attracted nearly so much attention. This paper, then, deals with case (2).

\* D. W. Taylor, *loc. cit.*, p. 115.

The most recent paper on the subject is by Dr. Bromwich,\* who gives the series solution in the following form :—

At a large distance,  $r$ , from the sphere, of radius  $a$ , the scattered wave is given by components in the directions of  $r$ ,  $\theta$ ,  $\phi$  respectively

$$\begin{aligned} X &= ca = 0, \\ Y &= c\gamma = \frac{\partial M}{\partial \theta} - \frac{1}{\sin \theta} \frac{\partial N}{\partial \phi}, \\ Z &= -c\beta = \frac{1}{\sin \theta} \frac{\partial M}{\partial \phi} + \frac{\partial N}{\partial \theta}, \end{aligned}$$

where

$$\begin{aligned} M &= -\sin \theta \cos \phi \frac{e^{-ikr}}{kr} \sum_1^{\infty} (-1)^n \frac{2n+1}{n(n+1)} \frac{S_n'(ka)}{E_n'(ka)} P_n'(\cos \theta), \\ N &= -\sin \theta \sin \phi \frac{e^{-ikr}}{kr} \sum_1^{\infty} (-1)^n \frac{2n+1}{n(n+1)} \frac{S_n(ka)}{E_n(ka)} P_n'(\cos \theta). \end{aligned} \quad (1)$$

The incident wave is of unit amplitude, is travelling along the axis  $\theta = 0$ , is polarised in the plane  $\phi = \frac{1}{2}\pi$ , and has wave-length  $2\pi/k$ . The time-factor  $e^{ikt}$  is omitted throughout.

$S_n(ka)$ ,  $E_n(ka)$  are the Riccati-Bessel functions which have been tabulated for integral values of  $n$  and  $ka$  up to 10 by the British Association Committee.†

Dr. Bromwich (*loc. cit.*) has transformed the series  $M$  and  $N$ , for  $ka$  large, by an application of Kelvin's "Method of stationary phase," and gets the approximate formulæ

$$\begin{aligned} Y &= \cos \phi (e^{-ikr}/kr)^{\frac{1}{2}} ka \exp(2ika \cos \tfrac{1}{2}\theta), \\ Z &= -\sin \phi (e^{-ikr}/kr)^{\frac{1}{2}} ka \exp(2ika \cos \tfrac{1}{2}\theta). \end{aligned} \quad (2)$$

These formulæ, the equivalents of which were published in the earlier papers of Nicholson, are for points not near to the axis  $\theta = \pi$  behind the sphere; the method does not seem to be capable of dealing with points near to this axis, nor does it seem suitable for obtaining a second approximation.

For points near to the axis  $\theta = \pi$ , Dr. Bromwich has applied another method, depending on the use of Green's theorem, and obtains

$$Y = iY_2 \cos \phi (e^{-ikr}/kr), \quad Z = iZ_2 \sin \phi (e^{-ikr}/kr), \quad (3)$$

where  $Y_2 = Z_2 = -kaJ_1(ka \sin \theta)/\sin \theta$ .

These points are not dealt with by Nicholson.

\* Bromwich, 'Phil. Trans.,' A, vol. 220, p. 187 (1920). See also Nicholson, 'Proc. London Math. Soc.,' vol. 9, p. 67 (1910); vol. 11, p. 277 (1912).

† Doodson, etc., 'B. A. Report,' p. 13 (1914); p. 39 (1916).

With a view to verification of these formulæ, numerical results\* have been calculated directly from the original series for  $ka = 10$ . Formulæ (2) were found to give quite good agreement for the range  $\theta = 0^\circ$  to  $90^\circ$ ; for the remainder of the range there was marked divergence. Formulæ (3) again give fair agreement for the range  $170^\circ$ – $180^\circ$ .

A paper by Prof. G. N. Watson† on the problem of case (1), mentioned above, suggested another method of attack. Watson transforms his series into another depending on the zeros of a Bessel function, and shows that this latter series converges very rapidly for large values of the argument, the first term alone giving a sufficient approximation.

It very soon appeared, as indeed might have been anticipated from the form of Dr. Bromwich's approximation, that it was not possible to transform the series M and N into others in Watson's manner, the contribution to the contour integrals from a large semicircle not tending to zero as the radius tends to infinity.

An example in Whittaker's 'Modern Analysis'‡ suggested a rather different procedure, whereby the series M and N are transformed into series depending on the zeros of Bessel functions, together with a contour integral along a "path of steepest descent." The contribution from the series is very small, and thus an approximation is given by the contour integral. This can be evaluated, after the manner of Debye,§ as an asymptotic series; the first term gives Bromwich's formulæ (2), and a second approximation can be obtained.

Comparison with the figures of Proudman shows an improved agreement over the range  $0^\circ$ – $90^\circ$ , but no better agreement over the remainder of the range.

The method breaks down as  $\theta$  approaches  $\pi$  for two reasons:

(1) Laplace's approximation for the Legendre function  $P_s(-\cos \theta)$  of high order  $s$  is no longer valid when  $\theta$  is so close to  $\pi$  that  $s(\pi - \theta)^3$  is small.

(2) Debye's simple approximations for Bessel functions of large argument are no longer valid when the order and argument are nearly the same.

The first fact shows itself in the series which we neglect for  $\theta$  not near to  $\pi$ ; this is found to involve exponentials with negative indices  $Ax^{\frac{1}{2}}(\theta - \pi)$ ,  $A$  being a positive constant, and the terms will no longer be negligible when  $x^{\frac{1}{2}}(\pi - \theta)$  is small ( $x$  is written for  $ka$ ).

This difficulty can be evaded by the use of Mehler's approximation for

\* Proudman, Doodson and Kennedy, 'Phil. Trans.,' A, vol. 217, p. 279 (1917).

† Watson, 'Roy. Soc. Proc.,' A, vol. 95, p. 83 (1918).

‡ 2nd edition, p. 145, Example 7.

§ Debye, 'Math. Annalen,' vol. 67, p. 535 (1909).

the Legendre function in terms of a Bessel function of zero order, and we find that the series M and N are now transformed into

- (a) A series depending on the roots of a Bessel function, this series being still negligibly small;
- (b) Several comparatively simple contour integrals which are negligible in the earlier case, but important now—approximations to these can easily be obtained;
- (c) A contour integral involving Bessel functions of order  $s$  and argument  $x$  along a curve in the  $s$ -plane which passes through the point  $s = x$ .

The evaluation of (c) is a matter of considerable complication and labour. In the first place, approximations to the various Bessel functions for nearly equal values of order and argument are required; some of these are given by Watson,\* but others had to be worked out on similar lines.

These approximations involve Bessel functions of orders  $\pm \frac{1}{3}$ ,  $\pm \frac{2}{3}$ , and the leading terms in (c) are found to depend upon definite numbers arising in the form of integrals of which the integrands are complicated expressions in these. To calculate these numbers, Dinnik's† Tables of the Bessel functions involved are of use, but they contain several misprints, and are not sufficiently detailed for small values of the argument, so that a considerable amount of arithmetic has been necessary.

The final result, for  $\theta$  near to  $\pi$ , is complicated; there is a term of order  $x^2$ , which is like Dr. Bromwich's but not identical with it, and there are further terms in  $x^{4/3}$ . Much better agreement is found with Proudman's figures for the range  $170^\circ$ – $180^\circ$ , but again the range of validity is little increased. For larger values of  $ka$ , the next terms in the approximation, involving presumably  $x^{2/3}$ , would be important; the labour necessary to obtain these by this method would be very great.

The intermediate range,  $90^\circ$ – $170^\circ$ , is thus still without adequate treatment.

(1) The series to which approximations are required are

$$M = -\sin \theta \cos \phi \frac{e^{-ikr}}{kr} \sum_1^\infty (-1)^n \frac{2n+1}{n(n+1)} \frac{S_n'(ka)}{E_n'(ka)} P_n'(\cos \theta),$$

$$N = -\sin \theta \sin \phi \frac{e^{-ikr}}{kr} \sum_1^\infty (-1)^n \frac{2n+1}{n(n+1)} \frac{S_n(ka)}{E_n(ka)} P_n'(\cos \theta).$$

With the notation of Watson,‡

$$S_n(x) = \psi_n(x) = \frac{1}{2} \{ \eta_n(x) + \zeta_n(x) \},$$

$$E_n(x) = -i\zeta_n(x),$$

where  $\eta_n(x) = (\frac{1}{2}\pi x)^{\frac{1}{2}} H_{n+\frac{1}{2}}^{(1)}(x)$ ,  $\zeta_n(x) = (\frac{1}{2}\pi x)^{\frac{1}{2}} H_{n+\frac{1}{2}}^{(2)}(x)$ ,

\* Watson, 'Proc. Camb. Phil. Soc.', vol. 19, p. 96 (1916).

† A. Dinnik, 'Archiv der Math. und Phys.' (3), vol. 22, p. 226 (1914).

‡ Watson, 'Roy. Soc. Proc.' A, vol. 95, p. 83 (1918).

and thus, since when  $n$  is a positive integer

$$P_n'(-\cos \theta) = (-1)^{n+1} P_n'(\cos \theta),$$

we have  $M = iA \cos \phi (e^{-ikr}/kr)$ ,  $N = iB \sin \phi (e^{-ikr}/kr)$ ,

where  $A = \sum_1^{\infty} \frac{2n+1}{n(n+1)} P_n'(-\cos \theta) \sin \theta \frac{\psi_n'(x)}{\zeta_n'(x)}$ ,

$$B = \sum_1^{\infty} \frac{2n+1}{n(n+1)} P_n'(-\cos \theta) \sin \theta \frac{\psi_n(x)}{\zeta_n(x)},$$

and  $x$  is written for  $ka$ .

(2) Following the example of Prof. G. N. Watson,\* we shall consider Bessel functions of which the order  $s$  is a complex quantity, and we shall use the transformation

$$s = x \cosh \gamma = x \cosh (\alpha + i\beta),$$

whereby the  $s$ -plane, slit along the real axis except between the points  $\pm x$ , is represented by the strip of the  $\gamma$ -plane between  $\beta = 0$  and  $\beta = \pi$ .

Fig. 1 represents the  $s$ -plane divided by the curves into regions

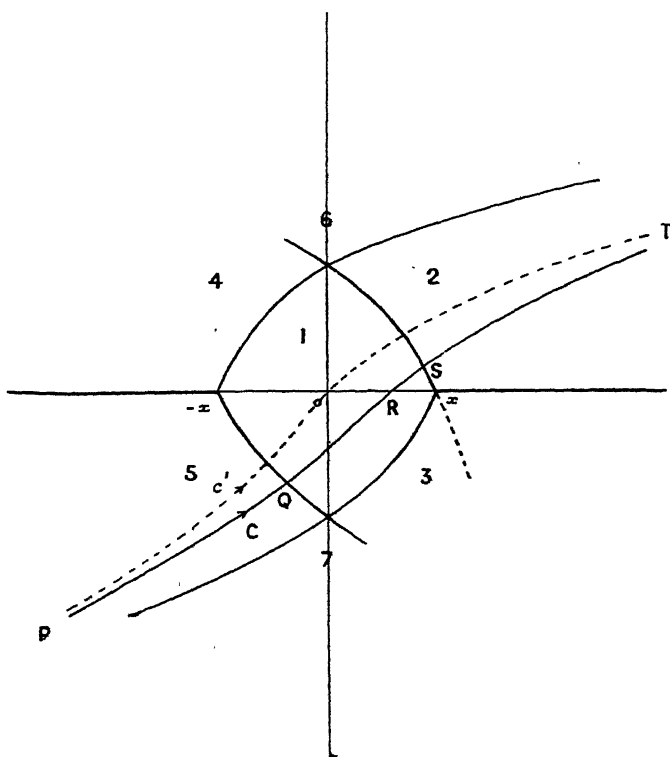


FIG. 1.

\* Watson, *loc. cit.*



(numbered 1-7) in which the Hankel-Bessel functions are given by different contour integrals, as shown in the Table on p. 93 of Watson's paper.

We shall require to apply the method of "steepest descents" to integrals involving

$$\exp [2x \{ \sinh \gamma - \gamma \cosh \gamma + \tfrac{1}{2} i (\pi - \theta) \cosh \gamma \}].$$

Suitable curves must pass through the point where this index is stationary, i.e., the point  $\gamma = \tfrac{1}{2} (\pi - \theta) i$ , and must have

$$I \{ \sinh \gamma - \gamma \cosh \gamma + \tfrac{1}{2} i (\pi - \theta) \cosh \gamma \} = \text{const.} = \cos \tfrac{1}{2} \theta.$$

This gives

$$\cosh \alpha \sin \beta - \alpha \sinh \alpha \sin \beta + \{ \tfrac{1}{2} (\pi - \theta) - \beta \} \cosh \alpha \cos \beta = \cos \tfrac{1}{2} \theta.$$

There is a double point at  $\alpha = 0, \beta = \tfrac{1}{2} (\pi - \theta)$ , the branches there having tangents  $\alpha = \pm \{ \beta - \tfrac{1}{2} (\pi - \theta) \}$ .

Along the branch touching  $\alpha = -\beta + \tfrac{1}{2} (\pi - \theta)$ , the real part of

$$\sinh \gamma + \{ \tfrac{1}{2} (\pi - \theta) i - \gamma \} \cosh \gamma$$

is negative; this branch goes off to infinity at  $(\infty, 0)$  and  $(-\infty, \pi)$ .

The corresponding curve, which we will call C, in the  $s$ -plane, passes

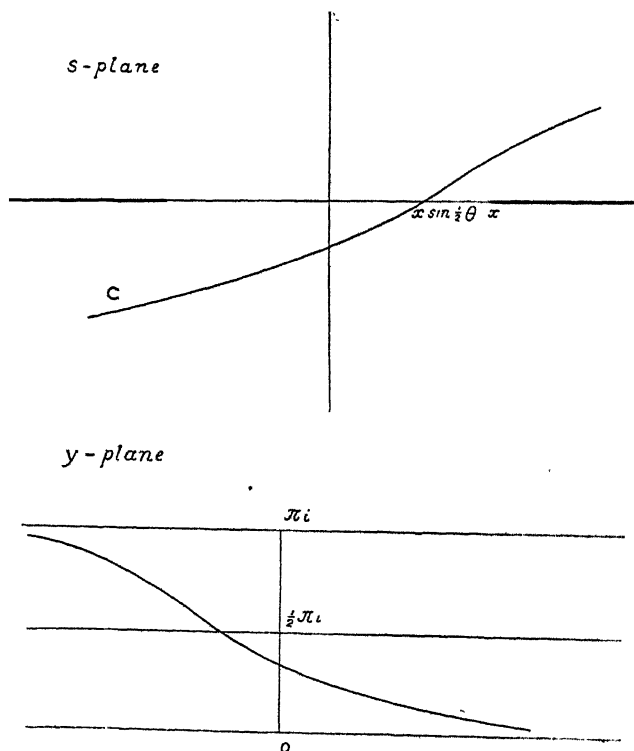


FIG. 2.

through the point  $s = x \sin \frac{1}{2}\theta$  of the real axis and goes off to infinity in directions parallel to the real axis but not asymptotic to it. These curves are shown in fig. 2.

(3) Now consider the contour integral

$$\int \frac{2s}{s^2 - \frac{1}{4}} \sin \theta P_{s-\frac{1}{2}}'(-\cos \theta) \frac{\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \frac{1}{e^{2s\pi i} + 1} ds, \quad (3.1)$$

taken round a circuit in the  $s$ -plane consisting of any curve  $C'$  symmetrical with regard to the origin and passing through it from the third quadrant to the first, together with a large semicircle below  $C'$ . The curve  $C'$  must not cross the boundary between the regions 6 and 2 and between 5 and 7; it must, in fact, behave at infinity like  $C$ .

Now in Watson's regions 5, 7, 3, 2 we have

$$\begin{aligned} H_s^{(1)}(x) &= S_s^{(1)}(x) - e^{-2s\pi i} S_s^{(2)}(x), & \frac{S_s^{(1)}(x) - e^{-2s\pi i} S_s^{(2)}(x)}{1 - e^{-2s\pi i}}, \\ &S_s^{(1)}(x), & S_s^{(1)}(x) - S_s^{(2)}(x); \\ H_s^{(2)}(x) &= S_s^{(2)}(x), & \frac{S_s^{(2)}(x) - S_s^{(1)}(x)}{1 - e^{-2s\pi i}}, & S_s^{(2)}(x) - S_s^{(1)}(x), & S_s^{(2)}(x), \end{aligned}$$

respectively, where when  $|\gamma|$  is not small and  $x$  is large,

$$\begin{aligned} S_s^{(1)}(x) &\sim e^{x(\sinh \gamma - \gamma \cosh \gamma) - \frac{1}{2}\pi i} \sqrt{\left\{ \frac{1}{2} \pi x \sin(-i\gamma) \right\}}, \\ S_s^{(2)}(x) &\sim e^{-x(\sinh \gamma - \gamma \cosh \gamma) + \frac{1}{2}\pi i} \sqrt{\left\{ \frac{1}{2} \pi x \sin(-i\gamma) \right\}}. \end{aligned}$$

$$\begin{aligned} \text{Thus} \quad \frac{2\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} &= 1 - e^{-2s\pi i} + \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)}, & \frac{(1 - e^{-2s\pi i}) S_s^{(2)}(x)}{S_s^{(2)}(x) - S_s^{(1)}(x)}, \\ &\frac{S_s^{(2)}(x)}{S_s^{(2)}(x) - S_s^{(1)}(x)}, & \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)}, \end{aligned}$$

respectively, and

$$\begin{aligned} \left| \left( \frac{1}{2} \pi x \right)^{\frac{1}{2}} S_s^{(1)}(x) \right| &\sim |\sinh \gamma|^{-\frac{1}{2}} e^P, \\ \left| \left( \frac{1}{2} \pi x \right)^{\frac{1}{2}} S_s^{(2)}(x) \right| &\sim |\sinh \gamma|^{-\frac{1}{2}} e^{-P}, \end{aligned}$$

where  $P$  is the real part of  $x(\sinh \gamma - \gamma \cosh \gamma)$ .

If  $s = R \mp i\phi$ ,  $\phi$  being a positive angle not greater than  $\frac{1}{2}\pi$ , we have when  $R$  is very large

$$|\sinh \gamma| \sim R/x,$$

$$P \sim R[\cos \phi (\log 2R/x - 1) - \phi \sin \phi].$$

Thus in 5,  $P$  is negative and of order  $R \cos \phi \log 2R/x$ .

As we move round the semicircle through 7 to 3 and 2,  $P$  increases, taking the value  $-\frac{1}{2}R\pi$  on the imaginary axis, vanishing on entering the fourth quadrant, and becoming positive in the remainder of 7 and in 3 with the approximate value  $R \cos \phi \log 2R/x$ . In 2,  $P$  is negative like  $-R \cos \phi \log 2R/x$ .

Thus  $\left| \frac{\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \right|$  is of order 1 on the semi-circle, except in the latter part of 7 and in regions 3 and 2, where it is of order  $e^{-2|P|}$ .

Also the approximate value of  $P_{s-\frac{1}{2}}'(-\cos \theta) \sin \theta$  for large values of  $s$  is  $(2s/\pi \sin \theta)^{\frac{1}{2}} \sin \{s(\pi - \theta) - \frac{1}{4}\pi\}$ , when  $\theta$  is not near to 0 or  $\pi$ .

Thus approximately  $|P_{s-\frac{1}{2}}'(-\cos \theta) \sin \theta| \sim (R/2\pi \sin \theta)^{\frac{1}{2}} e^{R(\pi - \theta) \sin \phi}$ . Hence the modulus of the integrand behaves like

$(2R/\pi \sin \theta)^{\frac{1}{2}} e^{-R(\pi + \theta) \sin \phi}$  in region 5 and the first part of 7,  
like  $(2R/\pi \sin \theta)^{\frac{1}{2}} e^{-R(\pi + \theta) \sin \phi - 2|P|}$  in the remainder of 7 and in 3,  
and like  $(2R/\pi \sin \theta)^{\frac{1}{2}} e^{-2|P|}$  in region 2.

Thus the integral round the large semi-circle tends to zero as its radius tends to infinity.

Next consider the poles of the integrand which lie within the contour. These consist of the zeros of  $\zeta_{s-\frac{1}{2}}(x)$ , and of the points  $s = n + \frac{1}{2}$ , where  $n$  is zero or a positive integer.

The residue at  $s = n + \frac{1}{2}$  ( $n > 0$ ) is  $-\frac{1}{2\pi i} \frac{2n+1}{n(n+1)} \sin \theta P_n'(-\cos \theta) \frac{\psi_n(x)}{\zeta_n(x)}$ .

The residue at  $s = \frac{1}{2}$  is  $\frac{1}{2\pi} \sin x e^{ix} \cot \frac{1}{2}\theta$ .

As regards the zeros of  $\zeta_{s-\frac{1}{2}}(x)$ , Watson\* has shown that these are simple and not on the real axis, and in fact lie near to the dotted curve proceeding from the point  $s = x$  into the fourth quadrant.

The residue at a zero  $s = \nu$  is

$$\frac{\nu}{\nu^2 - \frac{1}{4}} \sin \theta P_{\nu-\frac{1}{2}}'(-\cos \theta) \frac{\eta_{\nu-\frac{1}{2}}(x)}{[\partial/\partial s \zeta_{s-\frac{1}{2}}(x)]_{s=\nu}} \frac{1}{e^{2\nu\pi i} + 1}.$$

Thus we get, after some re-arrangement,

$$B = -i \sin x e^{ix} \cot \frac{1}{2}\theta$$

$$\begin{aligned} &+ 2\pi i \sum_{\nu} \frac{\nu}{\nu^2 - \frac{1}{4}} \sin \theta P_{\nu-\frac{1}{2}}'(-\cos \theta) \frac{\eta_{\nu-\frac{1}{2}}(x)}{[\partial/\partial s \zeta_{s-\frac{1}{2}}(x)]_{s=\nu}} \frac{1}{e^{2\nu\pi i} + 1} \\ &+ \int_{C'} \frac{2s}{s^2 - \frac{1}{4}} \sin \theta P_{s-\frac{1}{2}}'(-\cos \theta) \cdot \frac{\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \frac{1}{e^{2s\pi i} + 1} ds. \end{aligned} \quad (3.2)$$

(4) Next consider the contour integral

$$\int_{C'} \frac{s}{s^2 - \frac{1}{4}} \sin \theta P_{s-\frac{1}{2}}'(-\cos \theta) \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \frac{1}{e^{-2s\pi i} + 1} ds, \quad (4.1)$$

taken along the curve  $C'$ .

In region 5,  $\left| \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \right| \sim e^{-2R\pi \sin \phi}$ ; in region 2,  $\left| \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \right| \sim 1$ , and thus

\* Watson, *loc. cit.*, § 5.

the modulus of the integrand at each end of the curve behaves like  $(R/2\pi \sin \theta)^{\frac{1}{2}} e^{-R(\pi+\theta) \sin \phi}$  and the integral converges.

Now we have  $H_{-s}^{(1)}(x) = e^{s\pi i} H_s^{(1)}(x)$ ,  $H_{-s}^{(2)}(x) = e^{-s\pi i} H_s^{(2)}(x)$ , and thus  $\frac{\eta_{-s-\frac{1}{2}}(x)}{\zeta_{-s-\frac{1}{2}}(x)} \frac{1}{e^{2s\pi i} + 1} = \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \frac{1}{e^{-2s\pi i} + 1}$ , i.e., this expression is an even function of  $s$ . So also is  $P_{s-\frac{1}{2}}'(-\cos \theta)$ .

Hence the integrand is an odd function of  $s$  and the integral vanishes.

Adding to the equation (3.2), we get

$$B = -i \sin x e^{ix} \cot \frac{1}{2} \theta$$

$$\begin{aligned} & + 2\pi i \sum_{\nu} \nu / (\nu^2 - \frac{1}{4}) \sin \theta P_{\nu-\frac{1}{2}}'(-\cos \theta) \frac{\eta_{\nu-\frac{1}{2}}(x)}{(e^{2\nu\pi i} + 1) [\partial/\partial s \zeta_{s-\frac{1}{2}}(x)]_{s=\nu}} \\ & + \int_{C'} \frac{s}{s^2 - \frac{1}{4}} \sin \theta P_{s-\frac{1}{2}}'(-\cos \theta) \left[ \frac{2\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \frac{1}{e^{2s\pi i} + 1} + \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} \frac{1}{e^{-2s\pi i} + 1} \right] ds. \end{aligned} \quad (4.2)$$

The integral in equation (4.2) can be written

$$I_2 = \int_{C'} \frac{s}{s^2 - \frac{1}{4}} \sin \theta P_{s-\frac{1}{2}}'(-\cos \theta) \left[ \frac{2\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} - \frac{1}{e^{-2s\pi i} + 1} \right] ds \quad (4.3)$$

$$= \int_{C'} \frac{s}{s^2 - \frac{1}{4}} \sin \theta P_{s-\frac{1}{2}}'(-\cos \theta) \left[ \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} + \frac{1}{e^{2s\pi i} + 1} \right] ds. \quad (4.4)$$

The form (4.3) is suitable on the upper half of the curve, each part converging at this end; the form (4.4) is similarly suitable on the lower half.

Equation (4.2) has been proved for  $\theta$  not equal to 0 or  $\pi$ ; it can easily be seen that it holds for  $\theta = \pi$ , but it does not hold for  $\theta = 0$ , as the Legendre functions of non-integral order become infinite in this case.

(5) As regards the integral  $I_2$ , we note that  $\sin \theta P_{s-\frac{1}{2}}'(-\cos \theta)$  can be expressed as the sum of two terms

$$e^{[s(\pi-\theta)-\frac{1}{2}\pi]i} C_1 + e^{[-s(\pi-\theta)+\frac{1}{2}\pi]i} C_2,$$

where  $C_1$  and  $C_2$  can be expressed either as definite integrals or as asymptotic series in  $s^{-1}$  not involving exponentials.\*

Now consider the integral

$$I_2' = \int \frac{2s}{s^2 - \frac{1}{4}} e^{[-s(\pi-\theta)+\frac{1}{2}\pi]i} C_2 \cdot \frac{\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} ds,$$

the circuit consisting of  $C'$  and the large semi-circle below  $C'$ .

On the part of the semi-circle below the real axis, the integral tends to zero on account of the factor  $e^{-s(\pi-\theta)i}$ ; on the part above the real axis (in region 2) it tends to zero on account of the factor  $\frac{\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)}$ .

\*. Watson, 'Camb. Phil. Trans.,' vol. 22, pp. 291, 295 (1918).

$$\text{Thus } I_2' = -2\pi i \sum_{\nu} \frac{\nu}{\nu^2 - \frac{1}{4}} e^{[-\nu(\pi-\theta) + \frac{1}{2}\pi]i} C_{2(\nu)} \frac{\eta_{\nu-\frac{1}{2}}(x)}{[\partial/\partial s \zeta_{s-\frac{1}{2}}(x)]_{s=\nu}}. \quad (5.1)$$

The remaining part of  $I_2$  is

$$I_2'' = \int_{C'} \frac{s}{s^2 - \frac{1}{4}} \left\{ \frac{2\psi_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} e^{[s(\pi-\theta) - \frac{1}{2}\pi]i} - \frac{\sin \theta P_{s-\frac{1}{2}}'(-\cos \theta)}{e^{-2s\pi i} + 1} \right\} ds. \quad (5.2)$$

To get this in a form involving an integral along a "curve of steepest descent," we must consider the appropriate approximations for  $\psi_{s-\frac{1}{2}}(x)$  and  $\zeta_{s-\frac{1}{2}}(x)$  at various points of the curves C and C'. These curves pass through Watson's regions 5, 1 and 2, in all of which  $\zeta_{s-\frac{1}{2}}(x)$  is represented by  $(\frac{1}{2}\pi x)^{\frac{1}{2}} S_s^{(2)}(x)$ ; but in which  $\eta_{s-\frac{1}{2}}(x)$  is represented respectively by  $(\frac{1}{2}\pi x)^{\frac{1}{2}} \{S_s^{(1)}(x) - e^{-2s\pi i} S_s^{(2)}(x)\}$ ,  $(\frac{1}{2}\pi x)^{\frac{1}{2}} S_s^{(1)}(x)$  and  $(\frac{1}{2}\pi x)^{\frac{1}{2}} \{S_s^{(1)}(x) - S_s^{(2)}(x)\}$ .

Hence, as the integrand for which C is a suitable curve must contain the factor  $S_s^{(1)}(x)/S_s^{(2)}(x)$ , which of course is discontinuous at the points Q, S, where C crosses the boundary curves between the various regions, the integral involved must be (see fig. 1)

$$\int_P^Q \frac{s}{s^2 - \frac{1}{4}} e^{[s(\pi-\theta) - \frac{1}{2}\pi]i} C_1 \left[ \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} + e^{-2s\pi i} \right] ds + \int_Q^S \frac{s}{s^2 - \frac{1}{4}} e^{[s(\pi-\theta) - \frac{1}{2}\pi]i} C_1 \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} ds \\ + \int_S^T \frac{s}{s^2 - \frac{1}{4}} e^{[s(\pi-\theta) - \frac{1}{2}\pi]i} C_1 \left[ \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} + 1 \right] ds.$$

The remaining part of  $I_2''$  is, on reduction,

$$- \int_P^Q \frac{s}{s^2 - \frac{1}{4}} e^{-[s(\pi+\theta) + \frac{1}{2}\pi]i} C_1 ds - \int_S^T \frac{s}{s^2 - \frac{1}{4}} e^{[s(\pi-\theta) - \frac{1}{2}\pi]i} C_1 ds \\ + \int_{C'} \frac{s}{s^2 - \frac{1}{4}} \left[ \frac{e^{[s(\pi-\theta) - \frac{1}{2}\pi]i}}{e^{2s\pi i} + 1} C_1 - \frac{e^{-[s(\pi-\theta) - \frac{1}{2}\pi]i}}{e^{-2s\pi i} + 1} C_2 \right] ds.$$

This last integral can easily be seen to vanish over the large semi-circle below C', and thus the contribution of this last term is

$$\sum_{n=1}^{\infty} \frac{n + \frac{1}{2}}{n(n+1)} \sin \theta P_n'(-\cos \theta) - \frac{1}{2} \cot \frac{1}{2} \theta.$$

The series can easily be evaluated; its sum is  $-\frac{1}{2} \tan \frac{1}{2} \theta$ . This contribution is therefore equal to  $-\operatorname{cosec} \theta$ .

Thus

$$I_2'' = -\operatorname{cosec} \theta - \int_P^Q \frac{s}{s^2 - \frac{1}{4}} e^{-[s(\pi+\theta) + \frac{1}{2}\pi]i} C_1 ds - \int_S^T \frac{s}{s^2 - \frac{1}{4}} e^{[s(\pi-\theta) - \frac{1}{2}\pi]i} C_1 ds \\ + \int_C \frac{s}{s^2 - \frac{1}{4}} \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} \cdot e^{[s(\pi-\theta) - \frac{1}{2}\pi]i} C_1 ds \\ - 2\pi i \sum_{\nu} \frac{\nu}{\nu^2 - \frac{1}{4}} e^{[-\nu(\pi-\theta) + \frac{1}{2}\pi]i} C_{2(\nu)} \frac{\eta_{\nu-\frac{1}{2}}(x)}{[\partial/\partial s \zeta_{s-\frac{1}{2}}(x)]_{s=\nu}}. \quad (5.3)$$

This is for  $\theta$  not equal to 0 or  $\pi$ .

(6) Collecting the results so far obtained we get

$$B = -\frac{1}{2} \tan \frac{1}{2} \theta - \frac{1}{2} e^{2ix} \cot \frac{1}{2} \theta + 2\pi i \sum_{\nu} \nu / (\nu^2 - \frac{1}{4}) \cdot \eta_{\nu-\frac{1}{2}}(x) / [\partial / \partial s \zeta_{s-\frac{1}{2}}(x)]_{s=\nu} \\ \left[ \frac{e^{[\nu(\pi-\theta)-\frac{1}{2}\pi]i}}{e^{2s\pi i} + 1} C_1 - \frac{e^{-[\nu(\pi-\theta)-\frac{1}{2}\pi]i}}{e^{-2s\pi i} + 1} C_2 \right] - \int_P^Q \frac{s}{s^2 - \frac{1}{4}} e^{-[s(\pi+\theta)+\frac{1}{2}\pi]i} C_1 ds \\ - \int_S^T \frac{s}{s^2 - \frac{1}{4}} e^{[s(\pi-\theta)-\frac{1}{2}\pi]i} C_1 ds + \int_C \frac{s}{s^2 - \frac{1}{4}} \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} e^{[s(\pi-\theta)-\frac{1}{2}\pi]i} C_1 ds. \quad (6.1)$$

Precisely similar work applies to the series A; the only difference being that we have  $\eta_{s-\frac{1}{2}}'(x)$  and  $\zeta_{s-\frac{1}{2}}'(x)$  in place of  $\eta_{s-\frac{1}{2}}(x)$  and  $\zeta_{s-\frac{1}{2}}(x)$ , and consequently that the residue at  $s = \frac{1}{2}$  which arises in the equation corresponding to (3.2) gives a term  $\cos x \cdot e^{ix} \cdot \cot \frac{1}{2} \theta$ .

Thus

$$A = -\frac{1}{2} \tan \frac{1}{2} \theta + \frac{1}{2} e^{2ix} \cot \frac{1}{2} \theta + 2\pi i \sum_{\nu} \nu / (\nu^2 - \frac{1}{4}) \cdot \eta_{\nu-\frac{1}{2}}'(x) / [\partial / \partial s \zeta_{s-\frac{1}{2}}'(x)]_{s=\nu} \\ \left[ \frac{e^{[\nu(\pi-\theta)-\frac{1}{2}\pi]i}}{e^{2s\pi i} + 1} C_1 - \frac{e^{-[\nu(\pi-\theta)-\frac{1}{2}\pi]i}}{e^{-2s\pi i} + 1} C_2 \right] - \int_P^Q \frac{s}{s^2 - \frac{1}{4}} e^{-[s(\pi+\theta)+\frac{1}{2}\pi]i} C_1 ds \\ - \int_S^T \frac{s}{s^2 - \frac{1}{4}} e^{[s(\pi-\theta)-\frac{1}{2}\pi]i} C_1 ds + \int_C \frac{s}{s^2 - \frac{1}{4}} \frac{\partial / \partial x \{x^{\frac{1}{2}} S_s^{(1)}(x)\}}{\partial / \partial x \{x^{\frac{1}{2}} S_s^{(2)}(x)\}} e^{[s(\pi-\theta)-\frac{1}{2}\pi]i} C_1 ds. \quad (6.2)$$

(7) The next step is to investigate the co-ordinates of the points Q and S, with a view to determining the magnitudes of the terms in equations (6.1) and (6.2).

By actual plotting of the curves it is found that the imaginary co-ordinate of Q lies between  $0.6x$  and  $1.5x$ , while the imaginary co-ordinate of S lies between  $0.6x$  and  $0$ .

Hence when  $x$  is very large, it is seen that the integral from P to Q involves an exponential, the real part of whose index,  $(\pi + \theta)$  times the imaginary co-ordinate of Q, is large and negative. This integral is thus very small. The same is true of the integral from S to T, except when  $\theta$  is near to  $\pi$ .

In this latter case, S is given very approximately by

$$x \left( 1 - \frac{1}{24} \phi^2 + i \frac{\sqrt{3}}{24} \phi^2 \right), \text{ where } \phi = \pi - \theta.$$

The index of the exponential involved is thus  $-\frac{\sqrt{3}}{24} \cdot (\pi - \theta)^3$ , and thus the integral is no longer very small when  $(\pi - \theta)$  is of the order  $x^{-\frac{1}{3}}$ .

(8) We have next to consider the terms in A and B (equations 6.1, 6.2) arising from the zeros of  $\zeta_{s-\frac{1}{2}}'(x)$  and  $\zeta_{s-\frac{1}{2}}(x)$  respectively.

For  $\zeta_{s-\frac{1}{2}}'(x)$  the work is given by Watson,\* whose results are as follow.

\* Watson, 'Roy. Soc. Proc.' A, vol. 95, pp. 90-97 (1918).

The large zeros of  $\zeta_{s-\frac{1}{2}}'(x)$  are given approximately by the equation

$$x(\sinh \gamma - \gamma \cosh \gamma) - \frac{1}{4}\pi i = -(m + \frac{1}{2})\pi i,$$

where  $m$  is an integer large compared with  $x$ , and the corresponding value ( $\nu_m$ ) of  $\nu$  which makes  $\zeta_{\nu-\frac{1}{2}}'(x)$  have a simple zero is

$$\nu_m \sim (m + \frac{1}{4})\pi^2/2(\log m)^2 - (m + \frac{1}{4})\pi i/\log m.$$

The corresponding value of  $\gamma$  is

$$\gamma_m \sim -\log m + \frac{1}{2}\pi i.$$

These zeros lie in Watson's region 7, in which

$$\eta_{s-\frac{1}{2}}(x) = (\frac{1}{2}\pi x)^{\frac{1}{2}} \{S_s^{(1)}(x) - e^{-2s\pi i} S_s^{(2)}(x)\} / (1 - e^{-2s\pi i}),$$

$$\zeta_{s-\frac{1}{2}}(x) = (\frac{1}{2}\pi x)^{\frac{1}{2}} \{S_s^{(2)}(x) - S_s^{(1)}(x)\} / (1 - e^{-2s\pi i}).$$

Using the known approximations for  $S_s^{(1)}(x)$  and  $S_s^{(2)}(x)$  when  $|\gamma|$  is not small, we find that at the zero  $\nu_m$

$$\eta_{\nu-\frac{1}{2}}'(x)/[\partial/\partial s \zeta_{s-\frac{1}{2}}'(x)]_{s=\nu} \sim 1/2\gamma_m \sim -1/2 \log m.$$

Hence since the imaginary part of  $\nu_m$  is negative, the term in A arising from a large zero of  $\zeta_{s-\frac{1}{2}}'(x)$  is approximately

$$\frac{\pi i}{\nu_m \log m} [e^{-(m+\frac{1}{4})\pi(\pi+\theta)/\log m} C_1' - e^{-(m+\frac{1}{4})\pi(\pi-\theta)/\log m} C_2'],$$

which is very small as long as  $\theta$  is not nearly equal to  $\pi$ .

For the small zeros of  $\zeta_{s-\frac{1}{2}}'(x)$ , Watson\* obtains the approximate values

$$\nu = x + \rho x^{\frac{1}{2}} e^{-\frac{1}{2}\pi i},$$

where for the first three

$$\rho = 0.8083, 2.577, 3.83.$$

Using these results, we arrive at the conclusion that the first terms in the series in equation (6.2) contain exponentials with indices

$$-\frac{1}{2}\sqrt{3}\rho \cdot (\pi + \theta)x^{\frac{1}{2}} \text{ and } -\frac{1}{2}\sqrt{3}\rho (\pi - \theta)x^{\frac{1}{2}}$$

and are thus again small, for large values of  $x$ , except when  $\theta$  is nearly equal to  $\pi$ .

The work for the corresponding terms in B (equation 6.1) is very similar and gives similar results. As these terms are negligible, it is unnecessary to put down the details of the calculations.

(9) We have shown that for  $\theta$  not near to  $\pi$  (more accurately, as long as  $(\pi - \theta)x^{\frac{1}{2}}$  is large), we have approximately, neglecting terms containing exponentials with large negative indices,

$$A = -\frac{1}{2} \tan \frac{1}{2} \theta + \frac{1}{2} e^{2ix} \cot \frac{1}{2} \theta + \int_0^s \frac{s}{s^2 - \frac{1}{4}} \frac{\partial/\partial x \{x^{\frac{1}{2}} S_s^{(1)}(x)\}}{\partial/\partial x \{x^{\frac{1}{2}} S_s^{(2)}(x)\}} e^{[s(\pi-\theta)-\frac{1}{2}\pi]i} C_1 ds, \quad (9.1)$$

$$B = -\frac{1}{2} \tan \frac{1}{2} \theta - \frac{1}{2} e^{2ix} \cot \frac{1}{2} \theta + \int_0^s \frac{s}{s^2 - \frac{1}{4}} \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} e^{[s(\pi-\theta)-\frac{1}{2}\pi]i} C_1 ds. \quad (9.2)$$

\* Watson, *loc. cit.*, p. 97.

It remains to approximate to the integrals along the curve C. We must first write down the asymptotic expression for  $C_1$ . For the corresponding part of  $P_{s-\frac{1}{2}}(-\cos \theta)$  we have,  $|s|$  being large,

$$s^{[s(\pi-\theta)-\frac{1}{2}\pi]i} (2\pi s \sin \theta)^{-\frac{1}{2}} \left(1 + \frac{i}{8s} \cot \theta\right).$$

Differentiating, we get

$$C_1 \sim -i(s/2\pi \sin \theta)^{\frac{1}{2}} \left(1 - \frac{3i}{8s} \cot \theta\right). \quad (9.3)$$

The asymptotic expansions for  $S_s^{(1)}(x)$  and  $S_s^{(2)}(x)$  are given by Debye\*; he, however, uses  $i\tau_0$  where we have  $\gamma$ .

So long as  $|\gamma|$  is not small, which is true along the curve C when  $\theta$  is not near to  $\pi$ , we have

$$\begin{aligned} S_s^{(1)}(x) &\sim \exp \{x(\sinh \gamma - \gamma \cosh \gamma) - \frac{1}{4}\pi i\} \left\{\frac{1}{2}\pi x \sin(-i\gamma)\right\}^{-\frac{1}{2}} \\ &\quad \left[1 + \left(\frac{1}{8} - \frac{5}{24} \coth^2 \gamma\right) / x \sinh \gamma\right], \\ S_s^{(2)}(x) &\sim \exp \{-x(\sinh \gamma - \gamma \cosh \gamma) + \frac{1}{4}\pi i\} \left\{\frac{1}{2}\pi x \sin(-i\gamma)\right\}^{-\frac{1}{2}} \\ &\quad \left[1 - \left(\frac{1}{8} - \frac{5}{24} \coth^2 \gamma\right) / x \sinh \gamma\right]. \end{aligned}$$

After some reduction we get for the integral of equation (9.1), neglecting terms of relative order  $x^{-2}$ ,

$$\begin{aligned} (2\pi \sin \theta)^{-\frac{1}{2}} \int_C s^{-\frac{1}{2}} \exp \{2x(\sinh \gamma - \gamma \cosh \gamma) + ix \cosh \gamma (\pi - \theta) - \frac{1}{4}\pi i\} \\ \left[1 - \frac{3}{8} \frac{i \cot \theta}{x \cosh \gamma} + \frac{1/4 + 7/12 \coth^2 \gamma}{x \sinh \gamma}\right] ds \quad (9.4) \end{aligned}$$

and for equation (9.2),

$$\begin{aligned} -(2\pi \sin \theta)^{-\frac{1}{2}} \int_C s^{-\frac{1}{2}} \exp \{2x(\sinh \gamma - \gamma \cosh \gamma) + ix \cosh \gamma (\pi - \theta) - \frac{1}{4}\pi i\} \\ \left[1 - \frac{3}{8} \frac{i \cot \theta}{x \cosh \gamma} + \frac{1/4 - 5/12 \coth^2 \gamma}{x \sinh \gamma}\right] ds. \quad (9.5) \end{aligned}$$

The curve C is, as we anticipated, a "path of steepest descent" for our integrals, the "saddle-point" being at  $\gamma = \frac{1}{2}i(\pi - \theta)$ .

To evaluate them, we put

$$2 \sinh \gamma - 2\gamma \cosh \gamma + i(\pi - \theta) \cosh \gamma = 2i \cos \frac{1}{2}\theta - \tau^2.$$

Along C,  $\tau^2$  is real and positive, and the integrals involve  $e^{-\tau^2}$  multiplied

\* Debye, 'Math. Annalen,' vol. 67, p. 535 (1909); 'München Sitzungsber.,' Abh. 5 (1910).



by a factor which may be expanded in positive integral powers of  $\tau$ . The individual terms, of the type

$$\int_{-\infty}^{\infty} \exp(-x\tau^2) \tau^n d\tau,$$

are known integrals, and thus the evaluation may be effected to any term in the asymptotic series, though it becomes extremely laborious even to include terms of relative order  $x^{-2}$  (for which, of course, additional terms are required in the approximations, both for the Legendre and the Bessel functions).

The final results obtained are

$$A = -\frac{1}{2} \tan \frac{1}{2} \theta + \frac{1}{2} e^{2ix} \cot \frac{1}{2} \theta + \frac{1}{2} \operatorname{cosec} \frac{1}{2} \theta \exp(2ix \cos \frac{1}{2} \theta) \left\{ 1 + \frac{1}{2} i \sin^2 \frac{1}{2} \theta \sec^2 \frac{1}{2} \theta x^{-1} - \frac{1}{4} (5 \tan^2 \frac{1}{2} \theta + 7 \tan^4 \frac{1}{2} \theta) \sec^2 \frac{1}{2} \theta x^{-2} \right\}, \quad (9.6)$$

$$B = -\frac{1}{2} \tan \frac{1}{2} \theta - \frac{1}{2} e^{2ix} \cot \frac{1}{2} \theta - \frac{1}{2} \operatorname{cosec} \frac{1}{2} \theta \exp(2ix \cos \frac{1}{2} \theta) \left\{ 1 - \frac{1}{2} i \sin^2 \frac{1}{2} \theta \sec^2 \frac{1}{2} \theta x^{-1} + \frac{1}{4} (5 \tan^2 \frac{1}{2} \theta + 7 \tan^4 \frac{1}{2} \theta) \sec^2 \frac{1}{2} \theta x^{-2} \right\}. \quad (9.7)$$

Now, 
$$Y_1 + iY_2 = i \left[ \frac{\partial A}{\partial \theta} - \frac{B}{\sin \theta} \right],$$

$$Z_1 + iZ_2 = i \left[ \frac{\partial B}{\partial \theta} - \frac{A}{\sin \theta} \right].$$

On differentiating, it is found that the terms arising from the first two terms in equations (9.6), (9.7) vanish.

The values of the quantities that we are investigating are thus approximately, for  $\theta$  not near to  $\pi$ ,

$$Y_1 + iY_2 = \frac{1}{2} x \exp(2ix \cos \frac{1}{2} \theta) \left\{ 1 + \frac{1}{2} ix^{-1} \sec^3 \frac{1}{2} \theta - \frac{7}{4} x^{-2} \sin^2 \frac{1}{2} \theta \sec^6 \frac{1}{2} \theta \right\},$$

$$Z_1 + iZ_2 = -\frac{1}{2} x \exp(2ix \cos \frac{1}{2} \theta) \left\{ 1 + \frac{1}{2} ix^{-1} \cos \theta \sec^3 \frac{1}{2} \theta + \frac{7}{4} x^{-2} \sin^2 \frac{1}{2} \theta \sec^6 \frac{1}{2} \theta \right\}.$$

The following Table shows the values of  $Y_1$ ,  $Y_2$ ,  $Z_1$ ,  $Z_2$  calculated for  $kx = 1.0$  from the second approximation above. These are denoted by the letter A; and for comparison the corresponding values obtained by Proudman, Doodson, and Kennedy are also given under the letter B.

$$ka = 10.$$

$\theta$	$Y_1$		$Y_2$		$Z_1$		$Z_2$	
	A.	B.	A.	B.	A.	B.	A.	B.
0	1.76	2.02	4.67	4.88	-1.76	-2.02	-4.67	-4.88
10	2.16	2.21	4.52	4.57	-2.16	-2.32	-4.52	-4.36
20	3.12	2.90	3.92	4.16	-3.13	-3.16	-3.91	-3.93
30	4.34	4.26	2.51	2.80	-4.36	-4.31	-2.47	-2.51
45	4.78	4.98	-1.52	-1.85	-4.76	-4.79	1.61	1.64
60	0.60	0.20	-4.98	-5.09	-0.40	-0.40	4.99	4.98
70	-3.62	-3.27	-3.43	-3.83	3.81	3.85	3.25	3.34
80	-4.84	-4.41	1.37	1.96	4.67	4.72	-1.80	-1.75
90	-0.73	-1.40	5.00	5.09	0.02	0.14	-5.00	-5.19
100	4.53	4.51	2.33	0.97	-4.84	-4.92	-1.28	-1.32
110	3.47	4.22	-3.84	-3.27	-1.89	-2.45	4.65	4.81

(10) As a preliminary to considering values of  $\theta$  near to  $\pi$ , let us take the case in which  $\theta = \pi$ .

In this case we must differentiate our series before evaluating them. We have from § 1:—

$$Y = -\cos \phi \frac{e^{-ikr}}{kr} \sum_1^{\infty} (-1)^n \frac{2n+1}{n(n+1)} \left[ \frac{S_n'}{E_n'} \frac{\partial}{\partial \theta} \{ \sin \theta P_n'(\cos \theta) \} - \frac{S_n}{E_n} P_n'(\cos \theta) \right],$$

$$Z = -\sin \phi \frac{e^{-ikr}}{kr} \sum_1^{\infty} (-1)^n \frac{2n+1}{n(n+1)} \left[ \frac{S_n}{E_n} \frac{\partial}{\partial \theta} \{ \sin \theta P_n'(\cos \theta) \} - \frac{S_n'}{E_n'} P_n'(\cos \theta) \right]. \quad (10.1)$$

$$\text{Now } \frac{\partial}{\partial \theta} \{ \sin \theta P_n'(\cos \theta) \} = n(n+1) P_n(\cos \theta) - \cos \theta P_n'(\cos \theta).$$

Also, when  $\theta = \pi$ ,  $(-1)^n P_n(\cos \theta) = 1$ ;  $(-1)^n P_n'(\cos \theta) = -\frac{1}{2} n(n+1)$ . Hence, for  $\theta = \pi$ ,

$$Y = -\cos \phi \frac{e^{-ikr}}{kr} \frac{1}{2} (A+B), \quad Z = -\sin \phi \frac{e^{-ikr}}{kr} \frac{1}{2} (A+B), \quad (10.2)$$

where A and B denote the series

$$A = \sum_1^{\infty} (2n+1) \frac{S_n(ka)}{E_n(ka)}; \quad B = \sum_1^{\infty} (2n+1) \frac{S_n'(ka)}{E_n'(ka)}. \quad (10.3)$$

To the approximate evaluation of these series we now proceed.

In Watson's notation

$$A = i \sum_1^{\infty} (2n+1) \frac{\psi_n(x)}{\zeta_n(x)}; \quad B = i \sum_1^{\infty} (2n+1) \frac{\psi_n'(x)}{\zeta_n'(x)}.$$

By work which is exactly parallel to that of paragraphs 3, 4,

$$\begin{aligned} A &= -\sin x e^{ix} - 2\pi \sum_{\nu} \frac{\nu \eta_{\nu-\frac{1}{2}}(x)}{(e^{2\nu\pi i} + 1) [\partial/\partial s \zeta_{s-\frac{1}{2}}(x)]_{s=\nu}} + i \int_{C'} s \left[ \frac{\eta_{s-\frac{1}{2}}(x)}{\zeta_{s-\frac{1}{2}}(x)} + \frac{1}{e^{2s\pi i} + 1} \right] ds, \\ B &= -i \cos x e^{ix} - 2\pi \sum_{\nu} \frac{\nu \eta_{\nu-\frac{1}{2}}'(x)}{(e^{2\nu\pi i} + 1) [\partial/\partial s \zeta_{s-\frac{1}{2}}'(x)]_{s=\nu}} + i \int_{C'} s \left[ \frac{\eta_{s-\frac{1}{2}}'(x)}{\zeta_{s-\frac{1}{2}}'(x)} + \frac{1}{e^{2s\pi i} + 1} \right] ds. \end{aligned} \quad (10.4)$$

The series in (10.4) gives a negligible contribution when  $x$  is large, each term involving an exponential with large negative index.

As regards the contour integral, we may note that in this case, the curve  $C$  as defined in §2 degenerates into the boundary between regions 5 and 7, the boundary between regions 1 and 3, and the real axis from  $x$  to  $+\infty$ .

The expression which we shall have to integrate over  $C$  is, for  $A$ ,

$$\int s \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} ds.$$

The remainder, by a process similar to that of §5, is seen to be

$$\begin{aligned} & - \int_P^Q s e^{-2s\pi i} ds + \int_P^O \frac{s}{e^{2s\pi i} + 1} ds - \int_S^T \frac{s}{e^{-2s\pi i} + 1} ds + \int_O^S \frac{s}{e^{2s\pi i} + 1} ds \\ &= - \left[ \frac{ise^{-2s\pi i}}{2\pi} + \frac{1}{4\pi^2} e^{-2s\pi i} \right]_Q - 2 \int_O^T \frac{s}{e^{-2s\pi i} + 1} ds + \int_O^S s ds \\ &= \text{a negligible quantity} + \frac{1}{24} + \frac{1}{2} x^2, \end{aligned}$$

since  $S$  is the point  $x$ , and

$$\int_O^T \frac{s}{e^{-2s\pi i} + 1} ds = - \int_0^{\infty} \frac{y dy}{1 + e^{2y\pi}} = - \frac{1}{4\pi^2} \left\{ 1 - \frac{1}{2^2} + \frac{1}{3^2} - \dots \right\} = - \frac{1}{48}.$$

We have, finally, to approximate to  $\int_C s \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} ds$ .

Along the boundary between regions 5 and 7,  $|\gamma|$  is not small, and we have the approximation

$$\frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} = \exp \{ 2x \sinh \gamma - \gamma \cosh \gamma - \frac{1}{2} \pi i \}.$$

Since  $\sinh \gamma - \gamma \cosh \gamma$  is real and negative on this boundary, the contribution from this part of  $C$  involves an exponential with a large negative index and may therefore be neglected.

In region 1, approximations valid right up to the point  $x$  are :\*

$$S_s^{(1)}(x) = -\frac{2}{3}i \tanh \gamma \exp \{x(\sinh \gamma - \gamma \cosh \gamma) + \eta\} \\ \{e^{1/6\pi i} I_{-1/3}(\eta) + e^{-1/6\pi i} I_{1/3}(\eta)\},$$

$$S_s^{(2)}(x) = \frac{2}{3}i \tanh \gamma \exp \{-(x \sinh \gamma - \gamma \cosh \gamma) - \eta\} \\ \{e^{-1/6\pi i} I_{-1/3}(\eta) + e^{1/6\pi i} I_{1/3}(\eta)\},$$

where  $\eta = \frac{1}{3}x \sinh^3 \gamma \operatorname{sech}^2 \gamma$ , and the phase of  $\eta$  is to vanish when  $\gamma$  is real and positive.  $I$  is the modified Bessel function.

Thus the contribution from this part may be taken as

$$- \int s \exp \{2x(\sinh \gamma - \gamma \cosh \gamma) + 2\eta\} \frac{e^{1/6\pi i} I_{-1/3}(\eta) + e^{-1/6\pi i} I_{1/3}(\eta)}{e^{-1/6\pi i} I_{-1/3}(\eta) + e^{1/6\pi i} I_{1/3}(\eta)} ds.$$

The principal part of this integral, of course, arises for  $|\gamma|$  small. We now express everything in terms of  $\eta$ .

After some reduction, the term of the integral involving the highest power of  $x$  is found to be

$$- \int 3^{-1/3} x^{4/3} \eta^{-1/3} \frac{e^{1/6\pi i} I_{-1/3}(\eta) + e^{-1/6\pi i} I_{1/3}(\eta)}{e^{-1/6\pi i} I_{-1/3}(\eta) + e^{1/6\pi i} I_{1/3}(\eta)} d\eta.$$

Now the initial phase of  $\gamma$  (at  $x$ ) is  $\frac{2}{3}\pi$ , and hence the initial phase of  $\eta$  is  $2\pi$ , and thus, writing  $\eta = te^{2\pi i}$ ,  $t$  being a real positive quantity, the approximation to this part of the integral is

$$3^{-1/3} x^{4/3} e^{-1/3\pi i} \int_0^\infty t^{-1/3} \frac{I_{-1/3}(t) - I_{1/3}(t)}{I_{-1/3}(t) + e^{-1/3\pi i} I_{1/3}(t)} dt.$$

In an exactly similar manner, the approximation to the part arising from region 2 is found to be

$$3^{-1/3} x^{4/3} e^{-1/3\pi i} \int_0^\infty t^{-1/3} \frac{I_{-1/3}(t) - I_{1/3}(t)}{I_{-1/3}(t) + e^{1/3\pi i} I_{1/3}(t)} dt.$$

Adding, the final value of  $\int_C \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} ds$  is

$$3^{-1/3} x^{4/3} e^{-1/3\pi i} \int_0^\infty t^{-1/3} \frac{\{I_{-1/3}(t) - I_{1/3}(t)\} \{2I_{-1/3}(t) + I_{1/3}(t)\}}{I_{-1/3}^2(t) + I_{-1/3}(t) I_{1/3}(t) - I_{1/3}^2(t)} dt \\ = 3^{-1/3} x^{4/3} e^{-1/3\pi i} P, \text{ say.}$$

In the same way the approximation to the corresponding integral in B,

$\int_C s \frac{\partial/\partial x \{x^{1/2} S_s^{(1)}(x)\}}{\partial/\partial x \{x^{1/2} S_s^{(2)}(x)\}} ds$ , is found to be

$$- 3^{-1/3} x^{4/3} e^{-1/3\pi i} \int_0^\infty t^{-1/3} \frac{\{I_{-2/3}(t) - I_{2/3}(t)\} \{I_{-2/3}(t) + 2I_{2/3}(t)\}}{I_{-2/3}^2(t) + I_{-2/3}(t) I_{2/3}(t) + I_{2/3}^2(t)} dt, \\ = - 3^{-1/3} x^{4/3} e^{-1/3\pi i} Q, \text{ say.}$$

\* These approximations are not given explicitly by Watson, but can be obtained by application of the methods of his papers (*loc. cit.*, § 8, and 'Proc. Camb. Phil. Soc.', vol. 19, p. 96 (1916)).

The two integrals P and Q are definite numbers which can be calculated, to a sufficient approximation, by actually plotting the functions. For this purpose the tables of the modified Bessel functions of orders  $\pm \frac{1}{3}$ ,  $\pm \frac{2}{3}$ , as given by Dinnik,\* are of use, but additional figures, for small values of the argument, are also needed. These have been calculated directly from the series. For extremely small values of  $t$ , and for large values of  $t$ , the Bessel functions may be replaced by appropriate approximations, and thus it is only for intermediate values of  $t$ , say from  $t = 0.02$  to  $t = 2.2$ , that the curves need be plotted.

The final results are

$$P = 1.39, \quad Q = 1.24,$$

which are probably accurate to the second place of decimals.

(11) Collecting together our results, we have for the leading terms

$$A = \frac{1}{2}ix^2 + 1.39 \times 3^{-1/3} e^{1/6\pi i} x^{4/3},$$

$$B = \frac{1}{2}ix^2 - 1.24 \times 3^{-1/3} e^{1/6\pi i} x^{4/3}.$$

It is useful at this stage to compare the results obtained with those arrived at by direct arithmetical evaluation. In the paper of Messrs. Proudman, Doodson, and Kennedy, to which reference has already been made, the various series involved are calculated for  $x = ka = 10$ . It is possible to pick out what corresponds to the above series. In fact, the series A above is the same as the  $C + iD$  of equations (6), 2 of the paper quoted, and B is  $C' + iD'$ .

From Tables V-VIII, we conclude that for  $x = 10$ ,

$$A = 19.58 + i59.64, \quad B = -21.00 + i43.48.$$

The approximations above give

$$A = 17.98 + i60.38, \quad B = -16.04 + i40.76,$$

which is in close agreement, 10 not being very large compared with unity, as can be expected.

When, however, we come to take the sum of A and B, the terms in  $x^{4/3}$ , being very nearly equal and opposite, practically cancel, and the terms arising from the next approximation, involving presumably  $x^{2/3}$ , will become important. We find

$$\frac{1}{2}(A+B) = \frac{1}{2}ix^2 + 0.08 + 3^{-1/3} e^{1/6\pi i} x^{2/3},$$

\* A. Dinnik, 'Archiv der Math. u. Physik,' (3), vol. 22, p. 226 (1914). Some misprints may be noted. The correct values of  $I_{-1/3}(x)$ ,  $I_{-2/3}(x)$  are as follow :—

$x$ .	$I_{-1/3}(x)$ .	$x$	$I_{-2/3}(x)$ .
2.2	2.5626	2.8	3.7595
3.0	4.7754	8.0	415.01
6.0	66.55		

and, in the notation of the first paragraph,

$$Y_1 = Z_1 = -0.045 (ka)^{4/3},$$

$$Y_2 = Z_2 = -\frac{1}{2} (ka)^2 - 0.026 (ka)^{4/3}.$$

For  $ka = 10$ , these give

$$Y_1 = Z_1 = -0.97; \quad Y_2 = Z_2 = -50.57,$$

whereas the calculated values are

$$Y_1 = Z_1 = +0.71; \quad Y_2 = Z_2 = -51.56.$$

It would thus be desirable to carry the approximations to our contour integrals at least one stage further, but the labour involved seems to be prohibitive.

(12) There remains to discuss the case of  $\theta$  nearly equal to  $\pi$ . It is more convenient to differentiate the series before transforming them.

We get 
$$Y = -\cos \phi \frac{e^{-ikr}}{kr} [\Sigma_2 - \cos \theta \Sigma_4 - \Sigma_3],$$

$$Z = -\sin \phi \frac{e^{-ikr}}{kr} [\Sigma_1 - \cos \theta \Sigma_3 - \Sigma_4],$$

where

$$\Sigma_1 = \sum_1^{\infty} (-1)^n (2n+1) P_n(\cos \theta) \frac{S_n(ka)}{E_n(ka)},$$

$$\Sigma_2 = \sum_1^{\infty} (-1)^n (2n+1) P_n(\cos \theta) \frac{S_n'(ka)}{E_n'(ka)},$$

$$\Sigma_3 = \sum_1^{\infty} (-1)^n \frac{2n+1}{n(n+1)} P_n'(\cos \theta) \frac{S_n(ka)}{E_n(ka)},$$

$$\Sigma_4 = \sum_1^{\infty} (-1)^n \frac{2n+1}{n(n+1)} P_n'(\cos \theta) \frac{S_n'(ka)}{E_n'(ka)}.$$

The work of transformation is exactly parallel to that of the previous cases.

For  $\Sigma_1$  we have finally to approximate to

$$\int s P_{s-\frac{1}{2}}(-\cos \theta) \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} ds$$

taken over the same curve  $C$  as in the case of  $\theta = \pi$ .

The remainder is

$$-\int_P^Q s P_{s-\frac{1}{2}}(-\cos \theta) e^{-2s\pi i} ds - 2 \int_0^T s P_{s-\frac{1}{2}}(-\cos \theta) \frac{1}{e^{-2s\pi i} + 1} ds$$

$$+ \int_0^S s P_{s-\frac{1}{2}}(-\cos \theta) ds.$$

Of these the first may be neglected. Also  $S$  is the point  $s = n$ .

Since  $\theta$  is near to  $\pi$ , we may replace the Legendre function in the third integral by  $J_0(2s \cos \frac{1}{2}\theta)$ , and the integral becomes

$$\int_0^K s J_0(2s \cos \frac{1}{2}\theta) ds = \frac{1}{2}x \sec \frac{1}{2}\theta J_1(2x \cos \frac{1}{2}\theta),$$

which tends to  $\frac{1}{2}x^2$  as  $\theta$  tends to  $\pi$ .

Also the important part of the second integral is from  $|s|$  small, and so, swinging the contour round into the imaginary axis, we get

$$2 \int_0^\infty \frac{t J_0(2t \cos \frac{1}{2}\theta)}{1 + e^{2t\pi}} dt.$$

This can be evaluated as a series in  $\cos^2 \frac{1}{2}\theta$ , the coefficients involving Bernoulli's numbers. The first terms are

$$\frac{1}{24} + \frac{17}{960} \cos^2 \frac{1}{2}\theta + \dots$$

For the integral over C the process is practically as in paragraph 10, save that we have an additional factor  $J_0(2s \cos \frac{1}{2}\theta)$ .

Thus the result will be

$$0.964 J_0(2x \cos \frac{1}{2}\theta) e^{1/6\pi i} x^{4/3}.$$

Altogether the leading terms of  $\Sigma_1, \Sigma_2$  are

$$\Sigma_1 = \frac{1}{2}ix \sec \frac{1}{2}\theta J_1(2x \cos \frac{1}{2}\theta) + 0.964 J_0(2x \cos \frac{1}{2}\theta) e^{1/6\pi i} x^{4/3},$$

$$\Sigma_2 = \frac{1}{2}ix \sec \frac{1}{2}\theta J_1(2x \cos \frac{1}{2}\theta) - 0.86 J_0(2x \cos \frac{1}{2}\theta) e^{1/6\pi i} x^{4/3}.$$

In the series  $\Sigma_3$  the extra integrals are

$$-2 \int_0^T \frac{s}{s^2 - \frac{1}{4}} P_{s-\frac{1}{2}}'(-\cos \theta) \frac{1}{e^{-2s\pi i} + 1} ds + \int_0^K \frac{s}{s^2 - \frac{1}{4}} P_{s-\frac{1}{2}}'(-\cos \theta) ds,$$

of which the first gives

$$\frac{1}{48 \sin^2 \frac{1}{2}\theta} + \frac{1}{160} \cos^2 \frac{1}{2}\theta + \text{terms of higher degree in } \cos \frac{1}{2}\theta.$$

The second integral can easily be shown to be approximately

$$\operatorname{cosec}^2 \theta \{1 - J_0(2x \cos \frac{1}{2}\theta)\}.$$

The integral  $\int \frac{s}{s^2 - \frac{1}{4}} P_{s-\frac{1}{2}}'(-\cos \theta) \frac{S_s^{(1)}(x)}{S_s^{(2)}(x)} ds$  gives, on putting for  $P_{s-\frac{1}{2}}'(-\cos \theta)$  the approximate value  $\frac{1}{2}s \sec \frac{1}{2}\theta \operatorname{cosec}^2 \frac{1}{2}\theta J_1(2s \cos \frac{1}{2}\theta)$ , the expression  $\frac{1}{2x} \operatorname{cosec}^2 \frac{1}{2}\theta \sec \frac{1}{2}\theta J_1(2x \cos \frac{1}{2}\theta) \times 0.964 e^{-1/3\pi i} x^{1/3}$ .

Thus for the leading terms

$$\begin{aligned} \Sigma_3 = & -i \operatorname{cosec}^2 \theta \{1 - J_0(2x \cos \frac{1}{2}\theta)\} \\ & - 0.482 \operatorname{cosec}^2 \frac{1}{2}\theta \sec \frac{1}{2}\theta J_1(2x \cos \frac{1}{2}\theta) e^{1/6\pi i} x^{1/3}, \end{aligned}$$

and in a similar way

$$\Sigma_4 = -i \operatorname{cosec}^2 \theta \left\{ 1 - J_0(2x \cos \tfrac{1}{2} \theta) \right\} \\ + 0.43 \operatorname{cosec}^2 \tfrac{1}{2} \theta \sec \tfrac{1}{2} \theta J_1(2x \cos \tfrac{1}{2} \theta) e^{1/6 \pi i} x^{1/3}.$$

To compare with the figures for  $x = 10$ , we note that

$$\Sigma_1 = C + iD, \quad \Sigma_2 = C' + iD', \quad \Sigma_3 = A + iB, \quad \Sigma_4 = A' + iB',$$

in the notation of Proudman's paper.

The calculated values of the series give, for  $\theta = 170^\circ$ ,

$$\Sigma_1 = 5.65 + 37.47i, \quad \Sigma_2 = -5.12 + 28.84i, \quad \Sigma_3 = -7.08 - 24.20i, \\ \Sigma_4 = 6.25 - 18.04i,$$

while the above approximations give

$$\Sigma_1 = 6.7 + 37.2i, \quad \Sigma_2 = -5.9 + 29.9i, \quad \Sigma_3 = -6.03 - 24.3i, \\ \Sigma_4 = 5.38 - 17.7i.$$

The following Table shows the values of the series  $\Sigma_1, \Sigma_2, \Sigma_3, \Sigma_4$ , calculated from the above approximations for  $ka = 10$  in the range of values of  $\theta$  from  $170^\circ$  to  $180^\circ$ . The final figures for  $Y_1, Y_2, Z_1, Z_2$  (denoted by A), given therefrom by the formulæ

$$Y_1 + iY_2 = \Sigma_3 - \cos \theta \Sigma_4 - \Sigma_2, \\ Z_1 + iZ_2 = \Sigma_4 + \cos \theta \Sigma_3 - \Sigma_1,$$

are also shown, and for comparison the values obtained of these by Proudman (denoted by B).

$\theta$ .	$\Sigma_1$ .		$\Sigma_2$ .		$\Sigma_3$ .		$\Sigma_4$ .	
170	6.7 + 37.2i		-5.9 + 29.9i		-6.03 - 24.3i		5.38 - 17.7i	
172	10.24 + 44.69i		-9.13 + 33.51i		-7.01 - 26.30i		6.25 - 18.64i	
174	12.50 + 50.69i		-11.94 + 36.58i		-7.84 - 28.27i		6.99 - 19.39i	
176	15.86 + 56.05i		-14.15 + 38.72i		-8.46 - 28.71i		7.55 - 19.89i	
178	17.45 + 59.35i		-15.56 + 40.29i		-8.87 - 29.75i		7.91 - 20.06i	
180	17.98 + 60.38i		-16.04 + 40.76i		$-\frac{1}{2}\Sigma_1$		$-\frac{1}{2}\Sigma_2$	

$\theta$ .	$Y_1$ .		$Y_2$ .		$Z_1$ .		$Z_2$ .	
	A.	B.	A.	B.	A.	B.	A.	B.
170	-5.3	-7.12	-36.5	-35.28	4.5	6.59	-30.9	-31.67
172	-4.07	-4.76	-41.35	-41.0	2.95	4.7	-39.29	-38.0
174	-2.87	-2.33	-45.57	-45.6	2.29	3.0	-41.96	-43.9
176	-1.84	-0.23	-47.59	-49.3	0.13	1.6	-47.30	-48.4
178	-1.21	0.60	-49.99	-51.0	-0.68	0.8	-49.68	-51.0
180	-0.97	0.71	-50.57	-51.56	-0.97	0.71	-50.57	-51.56



### *On the Scattering of $\beta$ -Rays.*

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#### *Introduction.*

If a parallel pencil of homogeneous  $\beta$ -rays is made to fall on a thin sheet of any material the individual  $\beta$ -particles are deflected from their original path and the beam becomes scattered or diffuse. The deflections may be very considerable, even when the thickness of the material is far too small to produce any appreciable absorption either in the number or the energy of the particles in the beam. These deflections are generally ascribed to the action of the strong electric fields within the atoms of the scattering material, and measurements on the scattering of the rays afford a useful means of investigating the nature and magnitude of these atomic fields.

Experiments on the scattering of a beam of homogeneous  $\beta$ -rays were made some years ago by one of the writers\* with the object of obtaining an estimate of the number of electrons in the atoms of different elements. A theory of the phenomenon had been previously put forward by Sir J. J. Thomson† on the assumption, which was then generally accepted, that the atom consisted of a number,  $N$ , of negative electrons embedded in a sphere of positive electrification of atomic radius. On this view the deflection of a  $\beta$ -particle may be due either to the repulsion of the negative electrons in the atom, or to the attraction of the positive sphere. The probability of a particle suffering a large deflection from either of these causes could be shown to be negligibly small, and the actual observed deflections to be due to the cumulative effects of a large number of small deflections. Applying a theorem due to Lord Rayleigh it was shown that the probability that the deflection of the particle should be less than a given angle  $\phi$  was equal to  $1 - e^{-\phi^2/k^2}$  where  $t$  is the thickness of the scattering material, and  $k$  a constant which depends on the nature of the substance and the energy of the rays. Thus, if the rays after passing through the scattering substance were limited by a circular stop, whose radius subtended an angle  $\phi$  at the substance, the intensity of the radiation passing through the stop should be given by

$$I/I_0 = 1 - e^{-\phi^2/k^2}, \quad (1)$$

where  $I_0$  is the initial intensity of the beam.

\* J. A. Crowther, 'Roy. Soc. Proc.,' A, vol. 84, p. 226 (1910).

† Sir J. J. Thomson, 'Camb. Phil. Soc. Proc.,' vol. 15, p. 465 (1910).

If  $t_m$  is the thickness of the scattering foil necessary to cut down the radiation through the stop to half value, then for a given substance and given radiation

$$\phi^2/t_m = \text{constant.} \quad (2)$$

It was further shown that if  $T$  is the kinetic energy of the individual  $\beta$ -particle,  $e$  the charge on an electron,  $N$  the number of electrons in the atom, and  $n$  the number of atoms per cubic centimetre of the scattering material,

$$\phi = \frac{e^2}{mv^2} \left\{ \frac{384}{25} N_0 + \frac{\pi^2}{16} N^2 \right\}^{\frac{1}{2}} \sqrt{\pi n t_m}. \quad (3)$$

In the following year Sir Ernest Rutherford\* published a new theory of atomic structure in which he suggested that the positive charge in the atom, instead of occupying a sphere of atomic radius, was in reality confined to a nucleus of exceedingly small dimensions, so small, in fact, that it could be regarded as acting as a point-charge. This change of view was necessary to account for the very large deflections occasionally experienced by  $\alpha$ -particles during their passage through matter, and which the Thomson atom was incapable of explaining. The field due to such a central charge would produce deflections both in the  $\alpha$ - and the  $\beta$ -rays in comparison with which the deflections produced by the electrons in the atom would be negligible. The measured deflections in this case would be the large deflections produced by encounters with the positive nucleus of the atom. It was shown that until the material was so thick that half the particles had suffered one such deflection, the probability of a particle suffering two such deflections was negligibly small. The scattering was thus the result of single encounters of the particles with the nucleus of the atom. This may be called "single" scattering, to distinguish it from the multiple or "compound" scattering of Thomson's theory.

The probability that a particle shall suffer a deflection greater than  $\phi$  is, on the "single" scattering hypothesis, obviously proportional to the thickness of material it has to traverse. Thus the probability that the particle will still be included within an angle,  $\phi$ , after passing through a thickness,  $t$ , of the substance is  $1 - kt$ , or

$$I/I_0 = 1 - kt. \quad (4)$$

It can be shown that  $\phi^2/t_m$  is constant on the theory of single scattering. The experimental distinction between "single" and "compound" scattering lies, therefore, in the different relations given by the two for the variation in the intensity of the radiation through a fixed stop with increasing thickness of the scattering material. For single scattering the relation (4) is linear, for compound scattering it is a curve given by (1) with a double inflection.

\* Sir E. Rutherford, 'Phil. Mag.' [6], vol. 21, p. 669 (1911).

As the conditions for single scattering must ultimately cease to hold for thick foils (according to Rutherford's theory it holds until the radiation has been reduced to about half value) the transmitted radiation is bound eventually to decrease less rapidly than the linear relation, and the curve to become asymptotic to the axis of  $t$ . The possibility of discriminating between the two theories experimentally thus depends on the accuracy with which the initial portion of the curve can be determined. The experiments already referred to appeared to be in agreement with the theory of Sir J. J. Thomson, and values for  $N$  were deduced from (3) which showed that the number of electrons per atom was three times the atomic weight. The author's results were recalculated by Rutherford, on the nuclear theory, and gave values for  $N$  which were somewhat less than the atomic weight. The actual number of electrons per atom is now known with certainty to be equal to the atomic number of the elements, *i.e.*, approximately half the atomic weight. It was felt that, while the divergences between the experimental curves and relation (4) might be due to experimental imperfections, the differences between the calculated values of  $N$  and the corresponding atomic number were too large to be accounted for in this way. We were, therefore, very glad of the opportunity afforded by Sir Ernest Rutherford's very kind offer of a supply of radium emanation to investigate the matter in a more accurate way than had been possible with the comparatively weak source originally available.

The centre of interest had, of course, changed in the interval which had elapsed since the first paper was published. The nuclear theory of the atom is now well established, and the recent experiments of Chadwick, supported by a great mass of indirect evidence of many kinds, have proved that the charge on the nucleus, and, therefore, the number of electrons per atom, is exactly equal to the atomic number of the element. The discrepancies between the theory and the experiments on the scattering of  $\beta$ -rays, if proved to be genuine, would, therefore, be due to unexpected variations in the forces within the atom, and might throw new light on this very interesting point.

#### *Experimental Details.*

In principle the method of experiment was identical with that of the previous experiments, but many modifications have been made, suggested by experience and made possible by the greater intensity of the source, which have greatly increased the accuracy of the results. The present form of the apparatus is shown in fig. 1.

The source of the  $\beta$ -radiation is radium emanation contained in a thin-walled glass bulb of about 3 mm. diameter and placed at R. After passing through a stop,  $a_1$ , of 3 mm. diameter, the rays are formed into a magnetic

spectrum by passing between the poles of an electromagnet, the magnetic field being at right angles to the plane of the diagram. The path of the rays which actually reach the scattering material at P is defined by a series of stops,  $a_1, a_2, a_3$ . It will be seen that they have described a semicircle in the magnetic field, the radius of which in the actual experiments was 2.47 cm. The velocity of the  $\beta$ -particles employed can thus be determined from the applied magnetic field and the radius of the path. Calculation showed that with the apertures actually employed the extreme velocities of the emerging  $\beta$ -particles did not differ from the mean velocity by more than about 1 per cent. This  $180^\circ$  deflection of the rays, though not without its technical difficulties, produces a beam which is greatly superior in every way to that produced by the  $90^\circ$  deflection employed in the previous experiments.

On leaving the magnetic field the rays pass directly down the axis of a

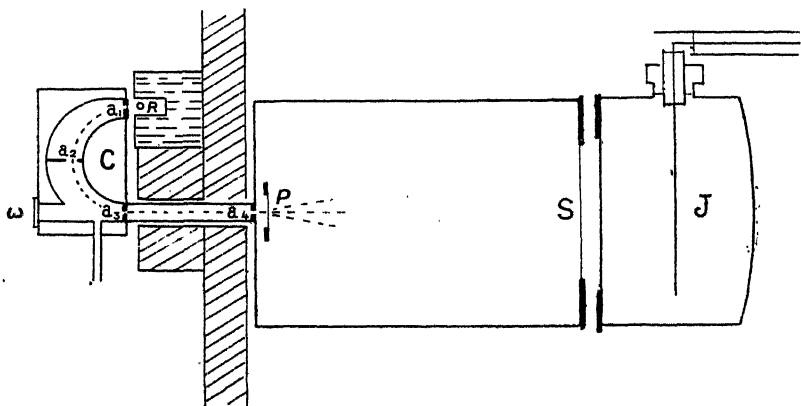


FIG. 1.

thick-walled iron tube, and are further screened from the magnetic field by large blocks of soft iron. After passing through another stop,  $a_4$ , also of 3 mm. diameter, the pencil falls normally on the scattering substance at P. In practice a number of these substances (or a number of different thicknesses of the same substance) were mounted on a frame moving in a fixed slide and operated from outside the chamber by a windlass, so that each in turn could be placed in the path of the rays. The diverging pencil produced by scattering in the substance at P could be limited by stops of different diameter placed at S. The intensity of the radiation passing through the stop was measured by means of an ionisation chamber, J.

In order to eliminate any scattering of the rays by air along their course, the apparatus was made airtight, the apertures  $a_1$  and S being closed by thin aluminium windows. The apparatus was filled with hydrogen and then

exhausted by a water pump. Experiment showed that, under these circumstances, there was no perceptible radiation outside the geometrical limits of the beam in the absence of any scattering substance at P. There was thus no scattering of the radiation by the residual gas, and no appreciable reflection of the primary radiation from the walls of the apparatus.

The ionisation produced in J was measured by a balance method, using the uranium oxide compensator, which has been fully described in previous papers.\* The compensator was again calibrated during the course of the present experiment, and the readings of the screw were found to be exactly proportional to the ionisation over the whole range employed. The position of balance was determined by a Wilson tilted electroscope, working at a sensitivity of about 90 divisions per volt. The connecting tubes were filled with sulphur, to reduce the loss of charge owing to ionisation of the air by  $\gamma$ -radiation.

The apparatus was screened as far as possible from the  $\gamma$ -radiation from the tube R by blocks of lead, but there was a very considerable residual effect. As the emanation decays to half value in 3.85 days, it was considered advisable to balance out the  $\gamma$ -ray effect by means of an auxiliary tube containing a small quantity of emanation placed near the compensator. The two emanation tubes were filled at the same time, and the balance when once established was thus automatically maintained. It may be worth mentioning in passing that it was found impossible to obtain a steady balance between the two tubes until some 10 hours had elapsed after filling the tubes.

The source, R, had generally an initial activity equivalent to that of 45 mgrm. of radium. The intensity of the  $\beta$ -radiation from this produced an ionisation in J which required eight complete turns of the compensator screw for compensation. A movement of the compensator screw of one-twentieth of a turn produced a sensible disturbance of the balance. Readings could thus be made to an accuracy of well within 1 per cent. of the initial intensity of the beam. The accuracy attainable is of course diminished as the emanation decayed. The source was generally replaced by a fresh one when its activity had fallen to about half value. The gradual decay in intensity of the  $\beta$ -radiation, which amounted to less than 1 per cent. per hour, caused no difficulties in obtaining a balance. Readings made at different times could easily be reduced to a standard value, as the radioactive constant of the emanation is known to an accuracy of at least 0.1 per cent.

In making the observations, the magnetic field was first applied so as to deflect the  $\beta$ -rays away from the scattering chamber, and an accurate balance obtained for the  $\gamma$ -ray effect alone. The field was then reversed, so as to

\* J. A. Crowther, *loc cit.*

deflect the rays on to the scattering substance, and a balance again obtained. The difference between the two compensator readings measured the intensity of the  $\beta$ -radiation transmitted through the stop. As a further precaution, both the balances were again verified. The process is tedious, the determination of a single point generally taking about  $1\frac{1}{2}$  hours. It is, however, by far the most accurate method of measuring small changes in an ionisation current, and readings could be repeated on different occasions to an accuracy of at least 1 per cent.

The scattering substances consisted of the thinnest foils of the elements concerned. Their thickness was measured by finding the mass of a known area of the foil. The average thickness was thus determined to an accuracy of 1 per cent. It is possible, however, that individual pieces of the foil might differ from the mean thickness, but the experimental results gave no evidence of this, although readings were made with different portions of the foil to test this point.

The magnetic field was measured by means of a fluxmeter, which was itself calibrated by means of a Hibbert standard, and also by a standard field employed by Mr. C. D. Ellis, and was found to be accurate to within 1 per cent. The kinetic energy,  $T$ , of the  $\beta$ -rays was calculated from the magnetic field and radius of curvature of the path, using the Planck-Einstein relation

$$T = Ve = m_0c^2 \left[ \frac{1}{\sqrt{1-\beta^2}} - 1 \right], \quad (5)$$

$V$  being the potential differences necessary to give the electron the energy  $T$ . Following the usual custom, the energy of the  $\beta$ -particle in this paper is given in terms of  $V$ , measured in volts.

#### *Variation of Scattering with Thickness of Material.*

The first point to be investigated was that of the relation between the intensity of the radiation transmitted through a stop of given aperture and the thickness of the scattering material. Bundles of one, two, three, four and five thicknesses of the same foil, cut from the same sheet, were mounted on the slide, and the intensity of the rays transmitted through the stop was measured for each of these bundles in turn. Experiments were made with stops subtending four different angles at the scattering substance, and both aluminium and gold were used in turn as the scattering substance. Some of the results are shown graphically in figs. 2 and 3, and specimens of the actual readings are given in Table I.

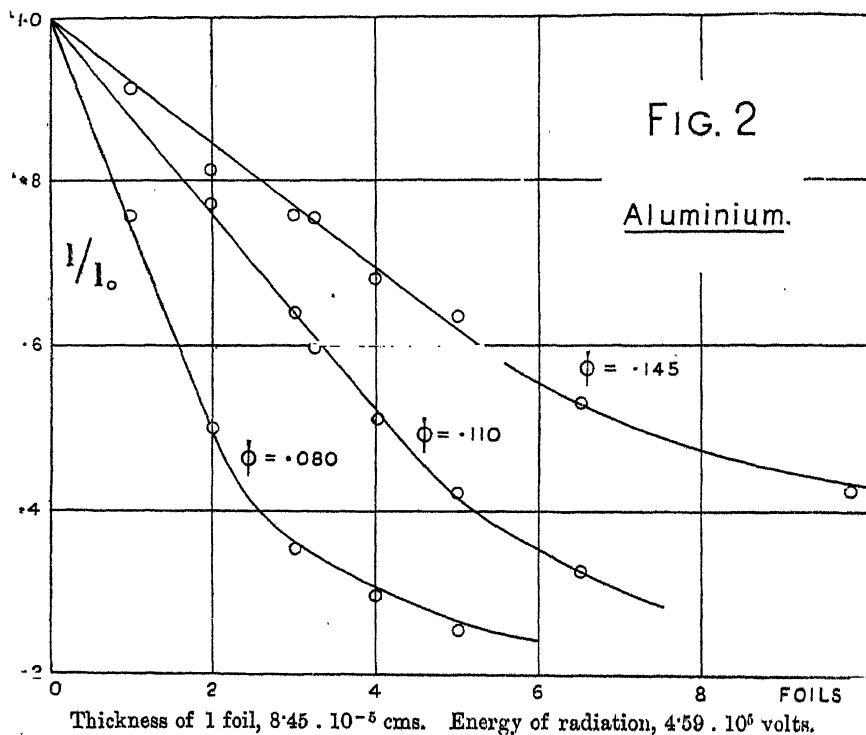
It will be seen that, in every case, the curve showing the relation between the transmitted radiation and the thickness of the absorbing material is

a straight line, until the radiation has fallen to at least half value. The intensity is thus given by

$$I/I_0 = 1 - \lambda t, \quad (4)$$

and not by equation (1). The scattering of the  $\beta$ -particles in the foils used in these experiments is therefore "single" scattering and not "compound."

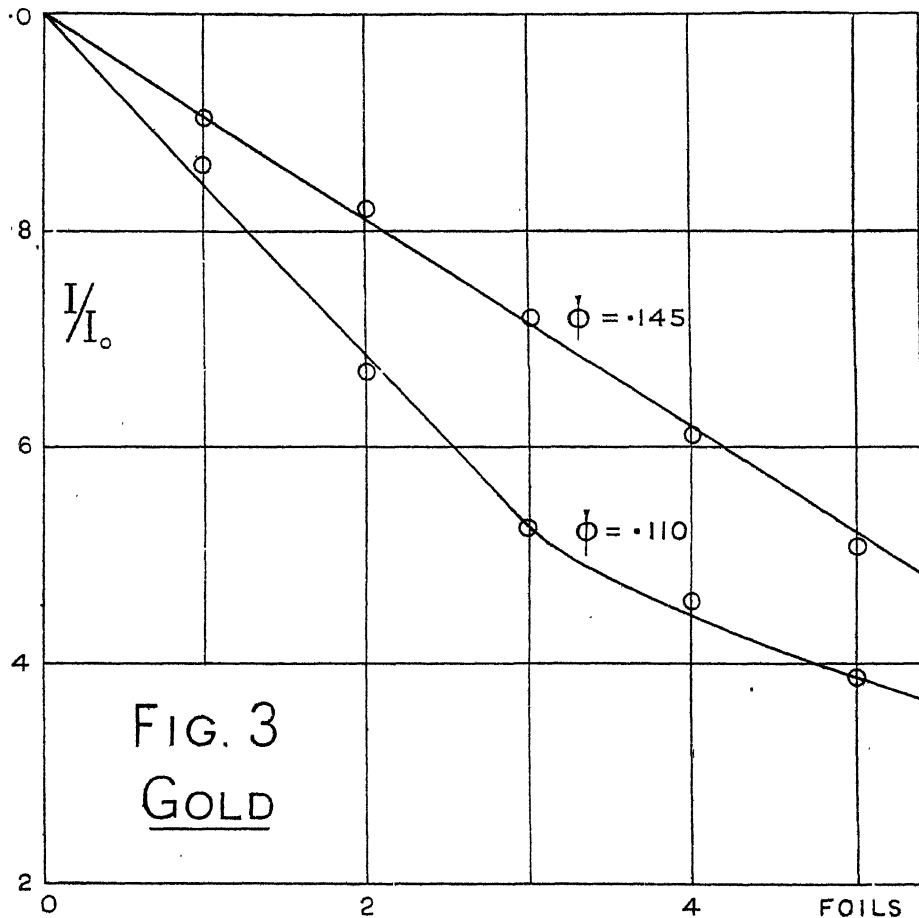
It will be seen that the initial flattening of the curve, which was so noticeable in the curves obtained in the previous experiments, and which is the criterion of compound scattering, is entirely absent from the present



curves. The departure of the original curves from the linear relation may be ascribed almost certainly to the fact that, owing to the small intensity of the source, it was necessary to use a beam of small, but still finite, divergence.

The matter could be tested experimentally by replacing the four stops by stops of larger aperture, say 5 mm. diameter, or more simply still by throwing the beam slightly out of alignment, so that its axis passed a little to one side of the centre of the stop S. Experiments were made under these conditions, and the experimental curves obtained always showed an initial flattening, sometimes in an exaggerated form.

These observations showed the importance of using a pencil of rays as nearly parallel as circumstances would permit. On the other hand, the intensity of the transmitted beam of radiation falls off very rapidly as the aperture of the stops is reduced. The stops actually used in the measurements recorded had a diameter of 3 mm. These stops allowed sufficient radiation to be transmitted to permit its intensity to be measured to an



accuracy of about 1 per cent., and at the same time, provided a pencil of sufficiently small divergence to render the error due to the divergence of the beam negligible, at any rate in the case of the larger stops. Since any error in centring the beam would produce similar effects to those produced by a divergence of the beam itself, the importance of the utmost accuracy in centring is apparent. The centring in these experiments was effected by sighting through the two stops,  $a_3$  and  $a_4$ , on the intersection of a pair of fine



Table I.—Typical Set of Measurements.

June 2, 1921. Gold: Thickness of one foil =  $8.48 \cdot 10^{-6}$  cm.  $\phi = 0.145$  radians. Energy of rays  $4.59 \cdot 10^5$  volts.

No. of foils.	Reading for $\gamma$ ray balance.	Time.	Reading for $\beta + \gamma$ ray balance.	Time.	Difference ( $\beta$ rays) I.	Time from Foil 0 ( $t$ ).	$e^{-\lambda t}$ .	$I/I_0 e^{\lambda t}$ .
0	2.670 2.665	9.40 A.M. 11.0 "	2.990 —	10.40 A.M. —	0.320 } 0.323 0.325 }	0 (10 A.M.)	1	1
1	2.540 2.540	11.20 " 12.0 P.M.	3.823 3.823	11.50 " 12.10 P.M.	0.283 }	2.0 hours	0.985	0.900
2	2.528 2.515	12.20 " 12.50 "	2.780 —	12.35 " —	0.252 } 0.258 0.265 }	2.5 "	0.981	0.822
3	2.460 2.460	1.45 " 2.25 "	2.635 —	2.15 " —	0.225 }	4.0 "	0.970	0.722
4	2.444 2.444	2.45 " 3.35 "	2.618 2.623	3.10 " 3.30 "	0.174 } 0.176 0.179 }	5.25 "	0.962	0.580
5	2.392 2.392	3.50 " 4.45 "	2.545 2.545	4.15 " 4.30 "	0.153 —	6.5 " —	0.953 }	0.508

wires, intersecting exactly at the centre of the stop S. For this purpose, a glass window,  $\omega$ , was made in the deflection chamber, C. In this way it was easy to ensure that axis of the beam was not more than 0.2 mm. from the centre of the stop.

The effect of a diverging beam on the intensity of the radiation transmitted through the stop can easily be demonstrated from general considerations. Let ABCD (fig. 4*a*) be the stop S, and with centre at O, and let P be a point within the cross-section of the unscattered beam. Describe a circle, AQCR, round P as centre, with radius equal to the radius of the stop. The

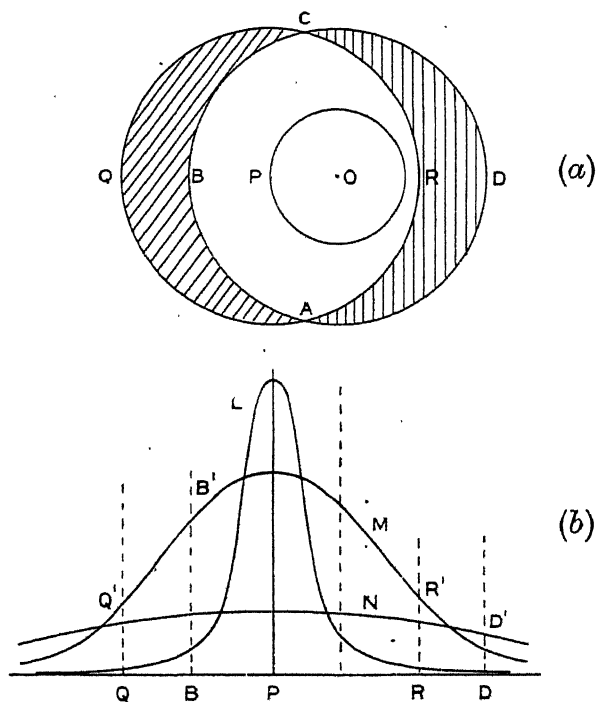


FIG. 4.

area AQCB is equal to the area ADCR. If P had been at O, the whole of the radiation within the circle AQCR would have passed through the stop. Owing to the divergence of the pencil, the radiation through the area AQCB is cut off by the stop, but the radiation through the area ADCR is transmitted in its place. The error due to divergence of the beam is measured by the difference in the radiation through these two areas. This will depend on the distribution of the scattered radiation about the axis of the beam.

We may assume that this distribution can be represented by probability curves, as indicated in fig. 4*b*, the width of the curve increasing as the

thickness of the scattering substance, and hence the most probable angle of scattering increases. Thus L represents the distribution curve for a very thin sheet of material, M for a greater thickness, and N for a still greater thickness. If PB, PQ, ... on this diagram represent the angles subtended at the scattering substance by the lines PB, PQ, ... in the other diagram, the error due to the obliquity of P will be the difference between the areas cut off from the curve between the ordinates at Q and B, and those at R and D, the area QBB'Q' being lost, and the area RDD'R' being added to the radiation through the stop. Now for very thin sheets of the scattering material (Curve L) this difference is negligible, and the initial portion of the curve will be practically unaffected by the obliquity of P. As the thickness of material increase (Curve M) the radiation lost becomes appreciably greater than that gained, and the experimental curves will fall appreciably below those for a narrow parallel pencil. The divergence of the beam produces a deviation from the linear relationship corresponding very closely with that observed in the earlier experiments. A consideration of curve N will show that the error becomes negligible again for thick foils.

We conclude then that the relation between the transmitted radiation and the thickness of the scattering material is a linear one for thin foils, the linear relation holding until approximately half the radiation has been deflected outside the stop. The results of the experiments with different materials and stops of different angle can be most conveniently recorded by giving the thickness,  $t_m$ , of material required to cut down the radiation through the stop to one half its initial intensity. In a few cases where the experimental curves seemed to deviate slightly from the linear relation before the intensity had been reduced to half, the half value thickness actually given in the Table of Results was obtained by producing the straight portion of the curve. The correction was, however, never more than a few per cent.

#### *Collected Results.*

The results obtained are summarised in Tables II and III. The whole of the observations in Table II were made with a deflecting magnetic field of 1110 gauss (HR = 2740 gauss-cm.), the corresponding velocity of the rays being  $2.552 \times 10^{10}$  cm./sec., and the energy of the particles  $4.59 \times 10^6$  volts. The first column indicates the nature of the scattering substance, together with its atomic number and atomic weight, the former being indicated by the clarendon type. Column II gives the angle of scattering, that is to say the angle subtended by the radius of the stop at the scattering substance. The third column gives the mass per unit area,  $x_m$ , of the foil required to cut down the radiation transmitted through the stop to half value. As the thickness of the

Table II.  
 $H\rho = 2740$  gauss-cm.  $\beta = 0.851$ .  $T/e = 4.59 \cdot 10^5$  volts.

I. Substance.	II. $\phi$ (radians).	III. $x_m$ (gm./cm. <sup>2</sup> ).	IV. $t_m$ (cm.).	V.		VI.		VII.	VIII.
				$\phi^2/t_m$	$\phi/\sqrt{t_m}$	$\phi^2/x_m$	$\phi/\sqrt{x_m}$	$\phi\sqrt{\Delta/x_m}$	$\phi\sqrt{\Delta/x_m} \times 1/N$ .
Al 13 27.1 .....	0.145 0.110 0.094 0.0803	$1.65 \times 10^{-3}$ $0.906 \times 10^{-3}$ $0.672 \times 10^{-3}$ $0.505 \times 10^{-3}$	$6.00 \times 10^{-4}$ $3.42 \times 10^{-4}$ $2.54 \times 10^{-4}$ $1.90 \times 10^{-4}$	35.0 35.3 34.7 34.0	5.92 5.94 5.89 5.83	12.7	3.57	18.6	1.43
Cu 29 63.6 .....	0.145 0.110	$1.67 \times 10^{-3}$ $0.945 \times 10^{-3}$	$1.86 \times 10^{-4}$ $1.05 \times 10^{-4}$	113 115	10.6 10.7	12.6	3.55	28.3	0.976
Ag 47 107.9 ...	0.145 0.110	$1.16 \times 10^{-3}$ $0.706 \times 10^{-3}$	$1.11 \times 10^{-4}$ $0.675 \times 10^{-4}$	189 179	13.75 13.4	18.1	4.25	44.2	0.940
An 79 197.2 ...	0.145 0.110	$0.843 \times 10^{-3}$ $0.507 \times 10^{-3}$	$4.37 \times 10^{-5}$ $2.63 \times 10^{-5}$	430 460	21.9 21.5	24.9	4.99	70.0	0.886
Celluloid 7 14.5	0.145 0.110	$3.17 \times 10^{-3}$ $1.71 \times 10^{-3}$	— —	— —	— —	0.60 7.10	2.57	9.96	1.42
Carbon 6 12 ...	0.145	$2.56 \times 10^{-3}$	—	—	—	8.20	2.86	9.9	1.65
Rice paper .....	0.110	$1.73 \times 10^{-3}$	—	—	—	7.0	—	—	—

Values in Columns VII and VIII for celluloid calculated from the formula  $C_{12}H_{18}N_2O_{16}$ , neglecting hydrogen. Thus mean A.W. = 14.5, and mean atomic No. = 7. Values for carbon obtained from carbonised paper.

Table III.

I.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Element.	$\phi$ (radians).	H $\rho$ .	E volts (T/e).	$t_m$ (toils).	$\phi/\sqrt{t_m}$ .	$f^2(\phi, \beta)$ .	$\frac{1}{2}mv^2/e$ .	$\phi/\sqrt{t_m} \times \frac{1}{2}mv^2/e$ .	$\phi/\sqrt{t_m} \times E$ .	$\phi/\sqrt{t_m} \times E/f(\phi, \beta)$ .
Au .....	0.110	4342	$10.3 \times 10^5$	13.3	$3.02 \times 10^{-2}$	2.41	$13.71 \times 10^{13}$	$4.19 \times 10^{12}$	$3.11 \times 10^4$	$2.00 \times 10^4$
	0.145	4101	8.23	15.3	3.71	2.34	11.37	4.22	3.05	1.99
	0.145	2742	4.59	5.15	6.39	1.92	6.97	4.45	2.98	2.11
	0.145	1694	2.11	1.70	11.1	1.45	3.59	3.99	2.34	1.94
Al .....	0.110	4342	10.3	14.3	2.91	2.41	13.71	3.99	3.00	1.93
	0.110	2742	4.59	4.05	5.46	1.81	6.97	3.81	2.51	1.86
	0.110	1870	2.51	2.31	7.24	1.28	4.15	3.01	1.81	1.60
C .....	0.110	4342	10.3	4.55	5.16	2.41	13.71	7.08	5.32	3.42
	0.110	2742	4.59	1.29	9.70	1.81	6.97	6.76	4.45	3.30
	0.145	2742	4.59	2.40	9.36	1.92	6.97	6.53	4.30	3.10
	0.145	1694	2.11	0.87	15.5	1.45	3.59	5.56	3.27	2.71

foils was always determined by weighing,  $x_m$  is the quantity actually measured. The actual thickness,  $t_m$ , given in Column IV is deduced from Column III, assuming the ordinary values for the density of the element. Column V gives the corresponding values of  $\phi/\sqrt{t_m}$  and  $\phi^2/t_m$ , and Column VI those of  $\phi^2/x_m$  and  $\phi/\sqrt{x_m}$ . The final column, VIII, gives the values of  $(\phi/N)\sqrt{A/x_m}$  where  $A$  is the atomic weight and  $N$  the atomic number. The significance of this column will be discussed later.

The value of the field in the experiments in Table II was chosen as giving the maximum intensity of  $\beta$ -radiation. Table III records the results of experiments made with rays of other velocities. The initial intensity of this radiation was generally small, and although this was partly counteracted by using a source of nearly twice the usual intensity the results cannot be relied on to the same order of accuracy as those in the previous Table.

Column 1 indicates the nature of the scattering material, Column 2 the angle of scattering, and Column 3 the value of HR in gauss-cm. Column 4 gives the corresponding energy of the individual  $\beta$ -particles,  $E$ , measured in volts, that is to say, their kinetic energy,  $T$ , divided by the charge,  $e$ , on the particles. Column 5 gives the values of  $t_m$ , the thickness which would be required to reduce the radiation through the stop to half value. Column 6 contains the corresponding values of  $\phi/\sqrt{t_m}$ , and Column 10 the values of  $E\phi/\sqrt{t_m}$ . The remaining columns in the Table will be referred to later.

### *The Nuclear Theory of Scattering.*

The deflection experienced by a particle passing in the neighbourhood of another fixed particle, which attracts or repels it with a force varying inversely as the square of the distance, can easily be solved by ordinary dynamical methods. Thus, if the nucleus of the atom can be regarded as acting as a point-charge of magnitude  $E_1$ , Rutherford showed that a particle carrying a charge,  $E_2$ , and moving with a kinetic energy,  $T$ , would be deflected through an angle,  $\phi$ , given by the relation

$$p = \frac{E_1 E_2}{2T} \cot \frac{\phi}{2} \quad (6)$$

where  $p$  is the perpendicular distance of the centre of the nucleus from the original direction of the moving particle.

If  $t$  is the thickness of the scattering material, and  $n$  the number of atoms per unit volume, the probability that the path of a single moving particle will pass within a distance,  $p$ , of any nucleus is  $\pi n t p^2$ , if  $t$  is small. The probability that it will not pass within this distance is therefore  $1 - \pi n t p^2$ , which is also the probability that its deflection will be less than  $\phi$ .

Hence, the fraction of the particles which are scattered through an angle less than  $\phi$ , is given by

$$I/I_0 = 1 - \pi n t p^2 = 1 - \pi n t \left( \frac{E_1 E_2}{2T} \right)^2 \cot^2 \frac{\phi}{2}. \quad (7)$$

This formula has been completely verified by Chadwick in the case of the scattering of the  $\alpha$ -particles by silver, copper, and gold, and the charge  $E_1$  on the nucleus has been shown to be equal to  $Ne$ , where  $N$  is the atomic number of the scattering element, to an accuracy of approximately 1 per cent.

Rutherford suggested that the same considerations should apply also to the scattering of the  $\beta$ -particles. In this case the charge  $E_2$  is simply  $e$ , and, putting  $E_1 = Ne$ , the radiation passing through a stop of angle  $\phi$  should be given by

$$I/I_0 = 1 - \pi n t \frac{N^2 e^4}{4T^2} \cot^2 \frac{\phi}{2}. \quad (8)$$

We have already seen that the relation between  $I/I_0$  and  $t$  is of this form.

The theory, however, requires some modification before it can be applied to the scattering of  $\beta$ -particles of the velocity used in the present experiments. The relation (6) was obtained on the assumptions that the mass of the particle remained constant, and that its energy was measured by  $\frac{1}{2}mv^2$ . These assumptions are sufficiently correct in the case of the  $\alpha$ -particles, but are not applicable to  $\beta$ -particles, which, commencing with a velocity of over two-thirds that of light, travel with ever increasing speed as they approach the attracting nucleus. This has already been pointed out by Darwin\* in connection with a theory of the absorption of the  $\beta$ -rays. For close distances of approach, the rapid increase in mass of the particles will cause them to move more slowly than if the mass had been constant. They are thus subjected to the attractive force of the nucleus for a longer time than would otherwise have been the case, and the deflection is thus increased. Darwin showed that, within a certain critical distance, the particle would actually be deflected into the nucleus, thus causing an absorption of the rays.

The relations obtained in the paper referred to were not immediately applicable to the present experiments. Mr. Darwin has very kindly worked out for us the complete theory, and has shown that, if  $p$  is the perpendicular distance from the nucleus of the undeflected path of the particle, and  $\phi$  the corresponding deflection, the latter is given by the relation

$$\beta \cot \psi = \tan \left\{ \pi - (\cos \psi) \frac{\phi + \pi}{2} \right\} \quad (9)$$

where

$$\operatorname{cosec} \psi = p/p_0 \quad \text{and} \quad p_0 = \frac{Ne^2}{c^2} \frac{\sqrt{1-\beta^2}}{\beta}.$$

\* C. G. Darwin, 'Phil. Mag.' [6], vol. 25, p. 201 (1913).

This equation replaces equation (6) of the simple theory, and (7) thus becomes

$$\frac{I}{I_0} = 1 - \pi n t p^2 \quad (10)$$

where  $p$  is now deduced from equation (9).

Probably the simplest way of comparing the experimental results with the theory is to regard the relations given by (9) as providing a correcting term to be applied to the simpler form of the theory. Let  $p'$  be the distance of approach necessary to produce a deflection,  $\phi$ , when the variation of mass with velocity is neglected, then  $p' = (Ne^2/2T) \cot \phi/2 = Ne^2/T\phi$  to an accuracy of about 0.2 per cent., since the maximum value of  $\phi$  in these experiments is about  $8^\circ$ . We may thus write (10) in the form

$$I/I_0 = 1 - \pi n t \frac{N^2 e^4}{T^2 \phi^2} \left( \frac{p}{p_1} \right)^2 \quad (11)$$

where

$$\left[ \frac{p}{p_1} \right]^2 = \frac{\operatorname{cosec}^2 \psi}{\{\beta^2/4(1 - \sqrt{1 - \beta^2})^2\} \cot^2 \phi/2} = f^2(\phi, \beta),$$

a function of  $\phi$  and  $\beta$  only, which can be determined by (9).

If  $t_m$  is the thickness of scattering material necessary to reduce the radiation through a stop, whose radius subtends an angle  $\phi$  at the substance, to half value

$$\pi n t_m \frac{N^2 e^4}{T^2 \phi^2} f^2(\phi, \beta) = \frac{1}{2}. \quad (12)$$

$f^2(\phi, \beta)$  thus represents the correction which, on the present form of the relativity theory, should be applied to the simpler theory to allow for variations in the mass of the  $\beta$ -particle. Values of the function under various experimental conditions are given in Table III, Column 7. In view of possible developments or modifications of the theory, however, we have thought it advisable to record in every case the actual "uncorrected" measurements, leaving the effect of applying the correcting factor to be discussed separately.

#### *Variation of $t_m$ with the Angle of Scattering.*

The values of  $\phi^2/t_m$  are given in Column V of Table II. It will be seen that to a first approximation the ratio is a constant for a given substance over the range of angles included in the Table. There is, however, a distinct difference to be noticed between the results for an element of low atomic weight, such as aluminium, and that for an element of high atomic weight, such as gold. The values of  $\phi/t_m$  for the former are constant within the limits of experimental error; but those for gold show a small but distinct



increase as the angle of the stop is increased. We shall show later that this increase becomes rapid for angles somewhat greater than those covered in the present experiments.

On the more complete theory represented by (12), the value of  $\phi^2/t_m f^2(\phi, \beta)$  should be constant for a given substance. The correcting factor  $f^2(\phi, \beta)$  varies very slowly with  $\phi$  over the range of angles included in the Table, and the correction only amounts to a few per cent. In the case of aluminium and copper the corrected values are distinctly less constant than the uncorrected values. The variations are, however, too small to provide a satisfactory test of the theory, and experiments over a wider range of angles will be required before definite conclusions can be drawn on this point.

#### *Variation of the Scattering with the Energy of the Rays.*

The deflection produced in a  $\beta$ -particle during a single encounter varies with the energy of the particle in a manner which depends on the law of force governing the encounter. Neglecting the variation of mass with velocity, the value of  $\phi/\sqrt{t_m}$  should be inversely proportional to the energy of the particle, if the force obeys the inverse square law, and inversely as the square root of the energy, if the law is that of the inverse cube of the distance. The former assumption corresponds to ordinary electrostatic action, the latter to magnetic action.

The problem is, however, complicated by the fact that the mass of the  $\beta$ -particle varies rapidly with its velocity, especially if the collision is a close one, and the correction to be applied for this variation is not as certain as might be desired. If, however, we accept (12) as giving the correct relation on the inverse square law of force, then  $\phi/\sqrt{t_m} f(\phi, \beta)$  should be inversely proportional to the energy, or  $(\phi/\sqrt{t_m}) E/f(\phi, \beta)$  should be constant, the value of  $E$  being deduced from the magnetic deflection  $H\rho$  by the relation (5).

Experiments were made with rays varying in energy from  $2.11 \times 10^6$  "volts" to  $1.03 \times 10^8$  "volts," using gold, aluminium and carbon as the scattering substances. The results are given in Table III. The actual experimental data will be found in Columns 3 and 5; Column 3 giving the value of  $H\rho$  for the rays employed and 5 the number of equal foils required to cut down the radiation to half value. The value of  $\phi/\sqrt{t_m}$  is contained in column 6.

Column 4 gives the energy of the particles in volts deduced from (5). The corresponding values of the correcting factor  $f^2(\phi, \beta)$ , are given in Column 7. The values of  $\phi/\sqrt{t_m} \cdot E$  are contained in Column 10 of the Table, and the values of  $\phi/\sqrt{t_m} \cdot E/f(\phi, \beta)$  in Column 11. The numbers in this column should therefore be constant on the present theories, if the law is that of the inverse squares.

The measurements for rays of very high and very low velocity are difficult owing to the small amount of such radiation emitted by the emanation tube. The values for gold must be regarded as very satisfactory under the circumstances, and may be taken as sensibly constant over the range of velocities employed, and at the particular angles employed. It is doubtful, however, whether the same can be claimed for the results for aluminium and carbon. For these elements the ratio does appear to increase steadily with increase in energy in each case, and the variation seems to be distinctly greater than the possible errors of experiment, as indicated by the experiments for gold. This would indicate either than the theory from which the correcting factor in Column 7 is calculated is inadequate in the case of these light atoms, or that the law of force in these cases is not accurately that of the inverse squares. As we shall show later, the collisions in the case of light elements are on an average much closer than those for a heavy element such as gold.

As a matter of interest the values of  $\frac{1}{2}mv^2/e$ , where  $m$  is the mass of the  $\beta$ -particle calculated from the Lorentz equation, are tabulated in Column 8, and the values of  $\phi/\sqrt{t_m} \cdot \frac{1}{2}mv^2/e$  in Column 9. The agreement of the figures in Column 9 is less close than that of the figures in Column 11.

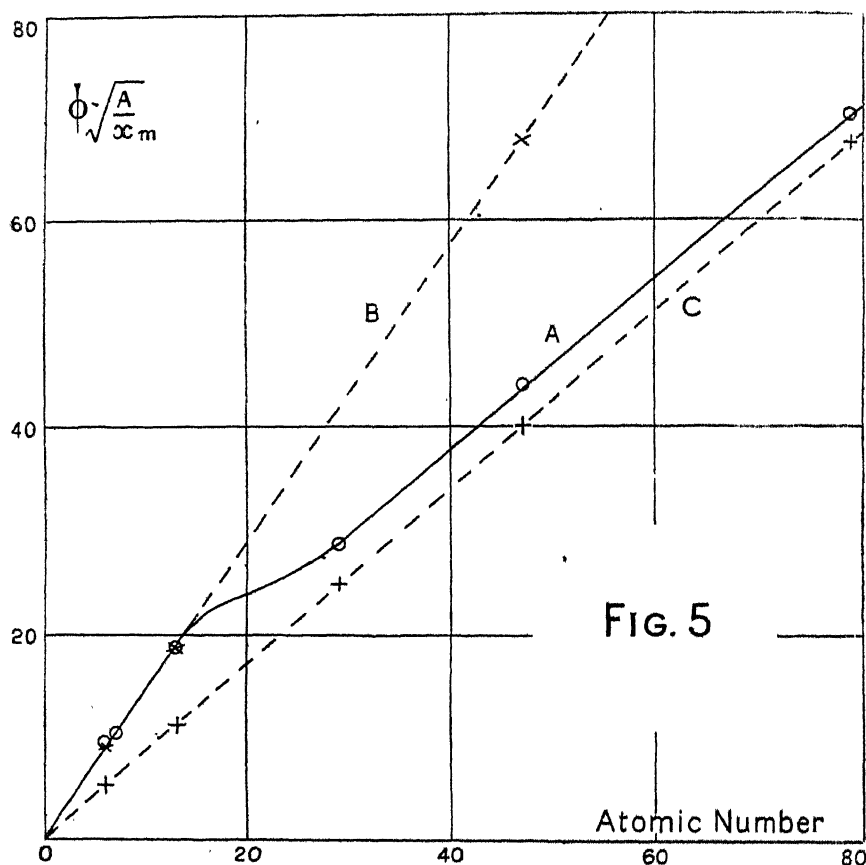
*Variation of the Scattering with the Atomic Number.*

It will be convenient, in discussing the relation between the scattering and the atomic number of the element producing it, to write the equations in a slightly different form. Let  $M$  be the mass of a hydrogen atom ( $= 1.65 \times 10^{-24}$  grm.) and  $A$  the atomic weight of the scattering substance. The number of atoms  $n$  per unit volume of the substance is therefore  $\Delta/MA$ , where  $\Delta$  is the density of the substance. Now, if  $x_m$  is the mass per unit area of the foil required to cut down the radiation to half value,  $x_m = \Delta t_m$ , whence  $n \cdot t_m = x_m/AM$ . Substituting this value for  $n \cdot t$  in the scattering relations (12) and (8), we see that, in either case, for the same stop, and for the same velocity of the radiation,  $\phi^2 A/x_m$  should be directly proportional to  $N^2$ , the square of the atomic number of the element, since  $f(\phi, \beta)$  depends only on  $\phi$  and  $\beta$ . Thus, on either form of the theory,  $(\phi^2/x_m) A/N^2$  should be constant. The last column of Table II, which contains the experimental values of this quantity, shows that this is very far from being the case, the scattering by the lighter elements being considerably greater than that produced by the heavier elements.

This is shown graphically by the full curve in fig. 5, in which the experimental values for  $\phi\sqrt{A/x_m}$  have been plotted against the atomic number. It will be seen that the departure from a linear relation is very considerable. There is thus a distinct discrepancy between the experimental results and

the nuclear theory of scattering in its present form, and this discrepancy is probably the most important point which emerges from the present experiments.

The nature and extent of the divergence may be best illustrated by



Variation of Scattering with Atomic Number.

A, present series,  $\phi = 0.145$  radians; B, Crowther (previous series),  $\phi = 0.314$  radians; C, theoretical values.

evaluating the theoretical equations for scattering (which contain no unknown constants), and comparing the results with the experimental values. So far we have neglected the effect of the electrons in the atom on the paths of the  $\beta$ -particles. It is easy to show that the effect should be relatively small. Assuming that the electron in the atom behaves as a fixed point charge of magnitude  $e$ , then in (6)  $E_2 = E_1 = e$ . Also, if  $N$  is the atomic number of the element, the total number of electrons per unit volume is  $Nn$ , and the fraction of the  $\beta$ -particles scattered through an

angle greater than  $\phi$  by collision with the electrons in the atoms is thus  $\pi \cdot Nnt(e^2/2T)^2 \cot^2 \phi/2$ . The fraction scattered outside the same angle by the nuclear collisions is  $\pi nt(Ne^2/2T)^2 \cot^2 \phi/2$ . Thus, taking into account both form of scattering, equation (8) becomes

$$\frac{I}{I_0} = 1 - \pi nt \frac{e^4}{4T^2} (N^2 + N) \cot^2 \phi/2. \quad (13)$$

The correction for electron scattering amounts to about 16 per cent. in the case of carbon, 7 per cent. for aluminium, and is negligible for the other elements investigated.

Thus, taking into account the variation of mass with velocity, (12) now becomes

$$\pi nt t_m \frac{e^4}{T^2 \phi^2} (N^2 + N) f^2(\phi, \beta) = \frac{1}{2} \quad (14)$$

which now includes both the nuclear and electronic scattering. This can easily be evaluated by writing  $nt = x_m/AM$  as before. The values of  $\phi\sqrt{A/x_m}$ , deduced from this equation, are given in Column 3 of Table IV, the experimental values being repeated, for the sake of comparison, in Column 2.

Table IV.

Element.	$\phi\sqrt{A/x_m}$ (observed).	$\phi\sqrt{A/x_m}$ (theoretical).	$k$ .
Gold.....	70.0	67.2	8.6
Silver .....	44.2	40.1	11.0
Copper .....	28.3	24.9	9.7
Aluminium .....	18.6	11.4	24.3
Carbon .....	9.9	5.4	17.0

It will be seen that in all cases the scattering actually observed is greater than that to be expected on the theory. The divergence is greatest in the case of the lighter elements, and decreases with increasing atomic number. Even in the case of gold, however, there is still a difference of about 5 per cent. between the two values. As the actually observed quantity is  $\phi^2/x_m$ , this would require an error in the observations of practically 10 per cent. The theoretical values are also indicated by the lower (broken) curve in fig. 5.

#### Discussion of Results.

It seems clear, from the figures and calculations of the previous section, that our present theories are inadequate to account for the observed scattering of a beam of  $\beta$ -particles during its passage through matter.

As the nature of the electrical force exerted by the nucleus seemed to have been so firmly established by experiments on the scattering of  $\alpha$ -particles, it was perhaps inevitable to consider whether, for some unknown reason, the deflections due to the electrons in the atom had been under-estimated. The theory that the electron is also a magneton, though not yet orthodox science, lends colour to the suggestion that in a collision between two electrons magnetic forces might be called into play which might result in a deflection considerably greater than that due to their electric charges. The relation between scattering and atomic number would then be of the form  $c(N^2 + kN)$  instead of  $c(N^2 + N)$  where  $k$  would be some constant greater than unity.

It is very doubtful whether a relation of this form is capable of representing the experimental results, which are shown graphically in the full curve in fig. 5. It is, of course, possible to choose a value for  $k$  which will give a smooth curve running fairly evenly among the experimental points on the graph. If we assume that the constant  $c$  has the value given by (12) the corresponding value of  $k$  can be calculated from the experimental data for the different elements. The results are given in Table IV. Taking 14 as an approximate mean value for  $k$  the calculated values for the scattering would agree with the observed values, to within the limits of experimental error, for all the elements except aluminium. For this element, however, the error in  $\phi/\sqrt{x_m}$  would amount to 10 per cent., implying an error in the actual observed value for  $x_m$  of as much as 20 per cent. As the value for aluminium is the one which has been determined with the greatest accuracy, and is the mean of a considerable number of closely concordant observations, it does not seem possible that an error of this magnitude can exist. Unless the scattering by aluminium is anomalous we must conclude that a formula of the type suggested cannot express the whole of the observations. It may, however, be worth noting, in this connection, that aluminium is the only one of the scattering substances employed which is paramagnetic, the magnetism being further increased in the case of the commercial metal by the appreciable amount of iron (usually about 1 per cent.) which it invariably contains.

It may be pointed out that if the value of  $k$  is as large as is required to account for the experimental values, the force between two electrons must be considerably greater than that given by Coulomb's law. Now with this value of  $k$  the scattering for the lighter elements would be mainly electronic, while that of gold would still be almost entirely nuclear. Thus, unless the law of force between the  $\beta$ -particle and an electron were the same as that between the  $\beta$ -particle and a nucleus, we should expect that the relation between the scattering and the energy of the  $\beta$ -particles should differ for light and for heavy elements. The results given in Column 11 of Table III do not

absolutely rule out this suggestion; but the observed variations are much less than would be expected if the forces were mainly magnetic.

Compton\* has recently published a magnetic theory of the deflection of the  $\beta$ -particles.† From a study of C. T. R. Wilson's very beautiful pictures of the actual tracks of  $\beta$ -particles through air, he concludes that the deflections of the particles are not random in direction, but that each particle has a kind of bias, which results in its deflections being all in the same direction. This is explained as being due to induced magnetism, produced in the scattering substance during the passage of the particle through it. The treatment in the original paper is obviously inadequate, being based on macroscopic considerations, whereas from the point of view of a  $\beta$ -particle the scattering substance is merely a space very sparsely studded with positive and negative charges. The author promises a reconsideration of the subject from this aspect, which he believes will lead to the same results; but this is not available at the time of writing.

The magnetic scattering suggested by Compton and others is clearly a multiple scattering. In fact, in its present form, it consists of a gradual bending of the track of the particles, due to a continuous force acting upon it. In its atomic form it would presumably be due to a large number of small deflections. If these were random in direction, the relation between the transmitted radiation and the thickness of scattering material would be given by an equation of the form of (3). In Compton's theory the deflections are all in the same direction. The form of the curve under these circumstances can easily be calculated, but it is obvious that, for the same value of  $t_m$ , the initial flattening of the curve would be even more pronounced than if the displacements were random. The shape of the experimental curves of figs. 2 and 3 make it clear that we are not dealing in the present experiments with inflections of this type.

#### *Comparison with Previous Results.*

It may be interesting at this stage to compare the results obtained in the previous paper† with the present experimental and theoretical values. A little calculation shows that the finite angle of the beam used in the previous work should not produce any very serious error in the values obtained for  $\phi^2/t_m$ . The velocity of the radiation used was rather greater than in the present experiments, and the angle of the stop was considerably larger ( $18^\circ$  as against  $8^\circ$  in the present work). We can, however, compare them with the present series by making use of the relations already discussed in previous

\* 'Phil. Mag.,' 1920.

† J. A. Crowther, 'Roy. Soc. Proc.,' A, vol. 84, p. 226 (1910).

sections. The values so obtained are given in Column II of Table V. It will be noticed that the values for carbon and aluminium are in excellent agreement with those obtained in the present experiments. This close agreement in the case of two elements makes it difficult to believe that the results obtained under identical conditions for the remaining elements can be seriously in error. Experiments now in progress, using stops of larger aperture, are, in fact, giving results for the heavier elements which confirm the general accuracy of the previous results.

Table V.

I.	II.	III.
Element.	$\phi/\sqrt{t_m}$ (old series).	$\phi/\sqrt{t_m}$ (new series).
Carbon .....	2.7	2.9
Al .....	5.8	5.9
Ag .....	20.8	18.6
Au .....	—	21.7
Pt .....	39.3	

Values given for energy of  $4.59 \cdot 10^5$  volts.

It will be seen, however, that the results for the heavier elements are considerably greater than those obtained in the present experiments. In fact the relation between  $\phi\sqrt{A/x_m}$  and  $N$  (indicated by the upper broken curve in fig. 5) is almost linear for the whole of the elements investigated.

#### *General Conclusions.*

Taking into account both series of experiments the results may be summarised by saying that, for light elements such as carbon and aluminium, the scattering as measured by  $\phi/\sqrt{t_m}$  is independent of  $\phi$  over the whole range of angles investigated (*i.e.*, from  $4^\circ$  to  $18^\circ$ ) but has a value which is nearly twice that to be expected on the current theories of the effect. On the other hand for heavy elements, such as gold or platinum, the scattering for very small values of  $\phi$  approximates closely to that to be expected from theoretical considerations, but increases rapidly with the angle, until for angles of  $18^\circ$  it is in agreement with the larger scattering shown at all the angles measured by the lighter elements. This is the main result which emerges from the observations.

The scattering of  $\beta$ -particles has so far been investigated only over a limited range both of angles and velocities, and it is clear that, in view of the unexpected nature of the results, a much more extensive survey of the subject

is required and this is now in progress. Attention may, however, be called to following points.

The distance  $p$  (see (6)) within which the original path of the particle must approach the centre of the deflecting nucleus in order to be deflected through an angle greater than  $\phi$ , decreases as the angle is increased. Thus the particles deflected out of the emerging beam will have made closer and closer approaches to the nucleus as the angle of the limiting stop is increased. The earlier experiments, therefore, refer to  $\beta$ -particles which have, on the whole, been much closer to the deflecting particles than those dealt with in the present series. The value of  $p$  in any given case can easily be deduced from the thickness of the scattering material. Thus, taking the values of  $t_m$  corresponding to the largest stop used in the present experiments, we find that for aluminium the undeflected paths of half the particles must have passed within a distance of  $6.5 \times 10^{-11}$  cm. of a nucleus. The corresponding value of  $p$  for gold is  $2.5 \times 10^{-10}$  cm. The collisions are, therefore, much closer for aluminium than for gold. In the earlier experiments, in which owing to the larger angle of stop, the values of  $t_m$  are greater, the average value of  $p$  for gold was approximately one-half that in the present series, and the paths of half the  $\beta$ -particles had approached within a distance of  $1.2 \times 10^{-10}$  cm. of a nucleus. Thus the results show that the scattering by gold changes from a value approximating closely to that given by the theory to the higher value corresponding to aluminium, when the average value of  $p$  changes from  $2.5 \times 10^{-10}$  cm. to  $1.2 \times 10^{-10}$  cm. The average values of  $p$  for aluminium are smaller than the latter value for all the angles investigated.

This method of viewing the data strongly suggests that some change is required in the present theory when the distance between the path of the  $\beta$ -particle and the deflecting particle is less than a certain critical value. Similar considerations (but with different constants) obviously also apply if we consider the collisions as taking place between the  $\beta$ -particle and the electrons in the atom. It is possible that the theory represented by the relation (9), for some reason not yet clear, does not adequately represent the motion of a  $\beta$ -particle which approaches very near to an atomic nucleus, acquiring in the process a velocity approaching within a very small fraction of the velocity of light. It is also possible that there may be some modification of the field at a certain distance from a nucleus or an electron, so as to produce a larger deflection of the  $\beta$ -particle than would be expected on the present theories. These suggestions are also supported by the results obtained on the variation of the scattering with the energy of the rays, where again the results were in much better agreement with the theory for gold, than for the lighter elements, where the collisions on an average were much closer. It is



hoped that the further survey now being made may indicate more clearly the nature of the modifications required.

We wish to express our warmest thanks to Prof. Sir Ernest Rutherford for his continued interest in these experiments and for his kindness in supplying the considerable quantities of emanation employed in the work. We are also indebted to Mr. Crowe for constructing and filling the emanation tubes.

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*Boundary Lubrication.—The Paraffin Series.*

By W. B. HARDY, Sec. R.S., and IDA DOUBLEDAY.

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(A Report to the Lubrication Committee of the Department of Scientific and Industrial Research.)

In what is often called complete lubrication, the kind of lubrication investigated by Towers and Osborne Reynolds, the solid surfaces are completely floated apart by the lubricant. There is, however, another kind of lubrication in which the solid faces are near enough together to influence directly the physical properties of the lubricant. This is the condition found with "dry" or "greasy" surfaces. What Osborne Reynolds calls "boundary conditions" then operate, and the friction depends not only on the lubricant, but also on the chemical nature of the solid boundaries. Boundary lubrication differs so greatly from complete lubrication as to suggest that there is a discontinuity between the two states. In the former the surfaces have the property of static friction, and the resistance is some inverse function of the viscosity of the lubricant. In complete lubrication static friction is absent and the resistance varies directly with the viscosity of the lubricant. Boundary lubrication is alone considered in this paper.

The enquiry is limited to the lubricating qualities of normal paraffins and their related acids and alcohols. The molecules of the substances employed, therefore, consist either of a simple chain of carbon atoms to which are attached atoms of hydrogen, or of such a chain loaded at one end with the hydroxyl group—OH, or the carboxyl group—COOH.

Attention was concentrated chiefly on three variables—the quantity of lubricant present, the composition of the solid faces, and the chemical constitution of the lubricant. The relations disclosed by the experiments are of surprising simplicity, whilst their interpretation is difficult. For this

reason the paper is divided into two parts, the first devoted to the results of experiment and the second to theory.

The Tables include values of the coefficient of friction for polished surfaces of bismuth. They are taken from an earlier paper, but it must be observed that a much higher order of accuracy was arrived at in the measurements with glass and steel than in those made previously with bismuth. The sensitiveness of the apparatus has been improved and very much greater care taken to secure purity in the substances used.

Of the chemicals used, some have been made by one of us (I. D.) and all have been specially purified until chemical tests failed to detect any impurity. Impurities present in too small amount to be detected by chemical means will produce a measurable effect on the very sensitive surfaces employed. It will be noticed that the value for undecane falls slightly below the curve for paraffins. The specimen had a marked odour, and, according to our experience with, *e.g.*, octane, the smell of normal paraffins decreases as purification proceeds. We believe, therefore, that there was a residual impurity of vanishingly small amount in the sample of undecane.

We are specially indebted to Prof. R. Robinson, F.R.S., for some of the higher paraffins and their related acids and alcohols.

#### PART I.—EXPERIMENT.

The experimental method employed to measure friction was that described in the earlier papers. The sliding piece or slider had a spherical surface, which was applied to a plane surface, the plate, both surfaces being highly polished. From the middle of the slider a short stem projected, from which a fine thread passed over a light pulley to a light pan for holding weights. The thread was adjusted so that the pull on the slider was parallel to the plane surface.

The use of a curved surface has the advantage that some measure of definiteness is given to the area of true contact. Two plane surfaces, trued as carefully as possible, touch only at a few points, as Budgett's experiments prove.

Both slider and plate were enclosed in a small chamber through which a current of air was passed, which had been purified by exposure (in order) to sulphuric acid, solid potash, calcium chloride, and phosphorus pentoxide, and finally passed through a column of glass-wool. In the earlier experiments the air was purified simply by bubbling through sulphuric acid and then passing it through a column of glass-wool, to trap any possible spray, but the vapour of sulphuric acid was found very seriously to interfere with the results by acting itself as a lubricant, and it was necessary to introduce solid potash to remove it. When the surfaces were covered only by an invisible

film of lubricant the vapour of sulphuric acid was found to lower the friction by no less than 17 per cent. Sulphuric acid is needed as a cleansing agent to remove organic impurities from the air.

Three solids were used, glass, steel and occasionally bismuth. The test of cleanliness, as was pointed out in an earlier paper, is the development of a high and constant value for friction. Each solid demands its own peculiar treatment to secure cleanliness, and when one embarks on a new solid, such as steel, it may be a month or more before a suitable method is found.

The "clean" state is one from which the grosser of the impurities which contaminate all naturally occurring surfaces have been removed. What remains, whether, for instance, there is left a film of condensed gas, is unknown. The state is, however, a perfectly definite one, in that it can be reproduced time after time with complete certainty. A plate of the glass used in these experiments is "clean" when its coefficient of friction is 0.94; the steel plates when clean gave the value 0.74. Other kinds of glass give values differing from 0.94. A negative may perhaps be ventured on. It is that "clean" surfaces are not the same as surfaces freshly produced by fracture. It is said that when steel is fractured under mercury the new surfaces amalgamate. "Clean" steel plates in clean air will not amalgamate.

*Glass plates* were cleaned by first washing with soap and water, rinsing under the tap, and allowing to dry by draining. They were then heated for about half an hour in a solution of chromic oxide in sulphuric acid, rinsed thoroughly under the tap (the plate being held with clean tongs) and allowed to drain. During draining, the lower edge of the plate rested upon two clean glass rods, the upper edge leaning against a clean glass bottle.

The glass sliders, being weighted with lead, could not be cleaned with chromic acid. They were, therefore, washed with soap and water, rubbed vigorously with the finger tips under a rapid flow of water until the "clinging" state was reached, and suspended in air until dry.

*Steel plates and sliders* were cleaned by washing with soap and water, rubbing vigorously with the finger tips in a stream of tap water until water wetted the entire surface, rinsing with perfectly dry pure alcohol, and allowing to drain in air. During the rinsing and draining processes the steel was not touched with the fingers at all, but held in tongs which had previously been cleaned by strong heating.

*Variables.*—The variables which have to be considered are the weight of the slider, the curvature of its surface, temperature, the thickness of the layer of lubricant, and the chemical nature of the lubricant and of the solids respectively. Of these one alone was not studied, namely, temperature, because the walls of the chambers which have been tried have given off

vapours at moderate temperatures in quantity sufficient completely to vitiate the measurements. A chamber of special design is being constructed which will, it is hoped, relieve us of this difficulty.

The fundamental law of sliding friction is usually known as Coulomb's\* law. As a matter of fact it was formulated 86 years earlier by Amontons;† we, therefore, propose to call it Amontons' law. According to it the friction is proportional to the weight of the slider and is independent of the area of contact. Coulomb regarded this law merely as an approximation and his view has been accepted by subsequent writers. We have made many measurements to verify the law, and they prove definitely that it is not an approximation, but an exact law, which holds so long as the surfaces, or rather the whole system, solid surfaces and lubricant, remain unchanged. Many solids suffer viscous flow from the pressure. This is the case when wood is used, and then the law ceases to hold. It is a rigid law for hard solids such as glass and hard steel.

According to Hertz's equation the area of contact varies as the cube root of the weight of the slider divided by its curvature. Careful measurements showed that the coefficient of friction ( $\mu$  = friction divided by weight) is independent of the weight and of the curvature. It is, therefore, independent of the area. The values of  $\mu$  are given in Tables I and II.

Table I.

Glass.					
Weight in grm. ....	21·63	31·64	41·63	51·63	61·63
Propyl alcohol.....	0·6321	0·6354	0·6301	0·6298	0·6352
Butyl     "     .....	0·6061	0·6042	0·6059	0·6076	0·6012
Amyl     "     .....	0·5821	0·5800	0·5833	0·5861	0·5847
Octyl     "     .....	0·5112	0·5126	0·5095	0·5093	0·5113
Heptylic     "     .....	0·4001	0·4018	0·4076	0·3982	0·3878
Caprylic     "     .....	0·3412	0·3392	0·3428	0·3413	0·3371
Heptane .....	0·6751	0·6703	0·6728	0·6741	0·6743
Octane .....	0·6551	0·6542	0·6508	0·6581	0·6548
Steel.					
Weight in grm. ....	15·46	25·46	35·47	45·47	55·49
Amyl alcohol .....	0·3658	0·3679	0·3708	0·3649	0·3651
Octyl     "     .....	0·2991	0·3032	0·2987	0·2999	0·3061

\* Coulomb, 'Mem. de l'Acad. Roy. des Sci.,' vol. 10, p. 161 (1785).

† Amontons, *ibid.*, p. 206 (1699).

Table II.—Steel.

Radius of curvature (cm.).....	14·70	3·58	1·78
Butyl alcohol .....	0·4018	0·4067	0·3917
Octyl " .....	0·3006	0·2991	0·2939
"Clean" .....	0·7408	0·7421	0·7427

*Influence of the Quantity of Lubricant.*

*Fluid Lubricants.*—Three methods of lubricating the surfaces were adopted:—

(1) A drop of lubricant was placed on the plate so that the slider stood in a pool of fluid. This is the *flooded* state.

(2) When a drop of a lubricant which has a sensible vapour-pressure is placed anywhere on a clean plate nothing detectable by the senses occurs. The drop to all appearances remains where it is placed without change. An invisible film, however, spreads from the neighbourhood of the drop so as to cover the whole plate. The presence of the film can be detected by the fall in friction. For reasons which will appear later (Appendix II) we call the invisible film the *primary film*, and the process by which it is formed *primary spreading*.

Obviously the invisible film would be subject to intense evaporation if the ordinary procedure were followed, in which a stream of clean air is passed through the chamber. This procedure was, therefore, modified as follows:—The lower part of the chamber was covered with a layer of fresh dry calcium chloride, and thoroughly washed out with a stream of dry air. The air stream was then cut off and it was found that clean plates remained completely uncontaminated in the chamber for 10 hours.

(3) When the lubricant has a sufficiently high vapour-pressure it can be deposited upon the surfaces by passing its vapour into the chamber. To accomplish this the stream of dry clean air was divided into two, one of which was bubbled through the lubricant whilst the other was led through a by-pass. The two streams were then led into a glass bulb provided with a device for thoroughly mixing them, and thence to the chamber. The proportion of the stream passing through the lubricant was varied by taps suitably placed and in this way the concentration of vapour in the chamber could be varied. In the case of one substance, ethyl alcohol, the concentration was determined directly by collecting samples of the stream as it entered the chamber and analysing them.

*Primary spreading* does not take place rapidly on a solid face. The friction falls slowly and finally reaches a steady value, it may be in an hour

or so, which is uniform over the whole surface. It is this value which is recorded. The mechanism of spreading is discussed in Appendix II.

In Table III the values of the coefficient of friction ( $\mu$  = friction divided by the weight) are given for flooding, for primary films, and for saturated vapour. The figures show that the friction is independent of the quantity of lubricant present, provided that there is enough to cover the surfaces with the invisible primary film.

Table III.

Lubricant.	Flooded.	Primary film.	Saturated vapour.
Glass.			
Ethyl alcohol.....	0·6512	0·648	0·6491
n-propyl alcohol .....	0·6301	0·6329	0·6283
n-butyl " .....	0·6061	0·6107	0·597
Amyl " .....	0·5853	0·5921	0·577
Caprylic " .....	0·5371	0·5356	—
Undecyl " .....	0·4450	0·4452	—
Butyric acid .....	0·5721	0·5793	0·5812
Valerianic acid .....	0·5259	0·5213	0·5309
Hexoic " .....	0·4653	0·4582	0·4648
Heptoic " .....	0·4051	0·4008	—
Caprylic " .....	0·3418	0·3412	—
Pentane .....	0·7102	—	0·7158
Hexane .....	0·6908	—	0·6913
Heptane .....	0·6753	—	0·6709
Octane .....	0·6557	—	0·6591
Steel.			
Butyl alcohol.....	0·3922	0·3906	0·3901
Amyl " .....	0·3751	0·3687	0·3716
Caprylic acid .....	0·2008	0·2073	—

It is obvious, since the primary film is in equilibrium with a drop of the parent fluid in a closed space, that its vapour pressure is the same as that of the free surface of the drop. Neglecting the very slight effect of the curvature of the drop in raising its vapour pressure we may, therefore, say that the vapour pressure of the primary film is that of a vapour saturated at the particular temperature. The critical value of friction, the value, that is to say, which is independent of the quantity of lubricant present is, therefore, that of faces so lubricated as to be in equilibrium with saturated vapour. The results obtained by using the lubricant as vapour confirm this view. The critical friction is also the lowest value which can be obtained in boundary friction.

The curves relating the coefficient of friction to the concentration of the vapour of ethyl alcohol are given in fig. 1, and the figures in Table IV. The concentration of the vapour is in gramme-molecules per litre.

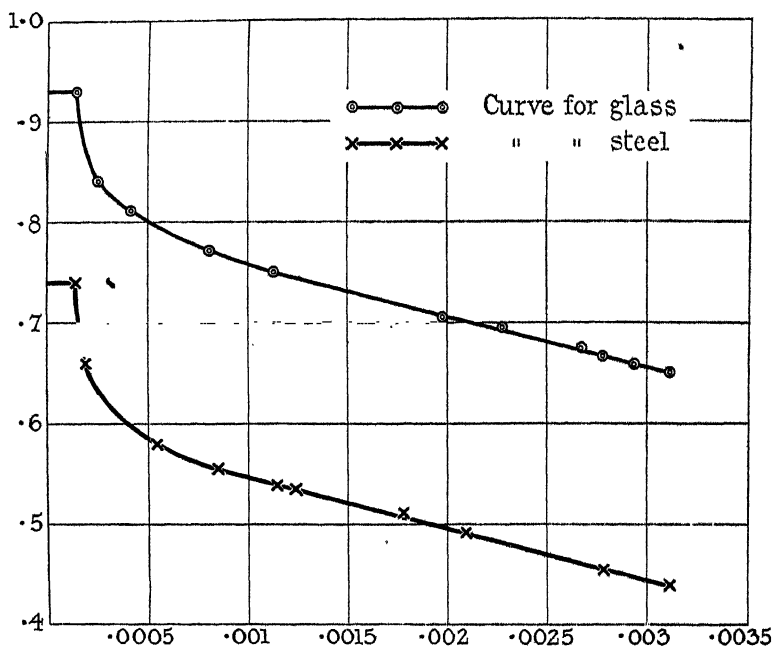


FIG. 1.—Abscissæ, number of gram-molecules of  $C_2H_5OH$  per litre of air.  
Ordinates, coefficient of static friction.

Table IV.—Ethyl Alcohol Vapour-Pressure Values.

Glass.		Steel.	
Grm.-mols. $C_2H_5OH$ per litre.	$\mu$ .	Grm.-mols. $C_2H_5OH$ per litre.	$\mu$ .
0.00014	0.94 (clean)	0.00013	0.74 (clean)
0.00025	0.841	0.00018	0.661
0.00042	0.816	0.00053	0.580
0.00081	0.773	0.00085	0.555
0.001127	0.752	0.001146	0.543
0.001973	0.705	0.001235	0.538
0.00228	0.696	0.001783	0.512
0.002675	0.675	0.002102	0.480
0.00278	0.668	0.002781	0.454
0.002936	0.660	0.00311	0.441
0.003111	0.651 (flooded value).		(flooded value).

The curves are straight lines save where the vapour-pressure is very low, when the results are liable to be upset by that degree of contamination from chance vapour which no amount of care in experimental procedure is likely to get rid of.

The fall in friction, therefore, is proportional to the concentration of chemical molecules of the lubricant in the gas phase, that is to say, each such molecule exerts the same influence as every other. The chances of any one molecule sticking to the solid surface will be proportional to the concentration in the gas phase, and therefore we may conclude that each chemical molecule in the film on the solid faces contributes an equal share to the fall in friction. This is not unlikely, since the fall in surface tension due to the presence of oleic acid on the surface of water is also proportional to the number of molecules of the acid per unit area.\*

The most important features of these curves connecting vapour-pressure and the coefficient of friction are : (1) that they do not if prolonged meet the  $\mu$ -axis at the clean value, though the measurement made with the lowest vapour pressure coincides with this value ; and (2) that the curves are parallel to each other over the linear portion.

The clean value obviously must form one end of the curves and in the figure they are continued so as to cut the  $\mu$ -axis at this value. The first part of each curve is, therefore, horizontal. That is to say, a finite concentration of lubricant on the surface is needed to produce any fall in friction. It is well known, since Rayleigh pointed it out, that a finite concentration of a substance spread on the surface of water is needed to cause a fall in surface tension. Rayleigh suggested that this critical concentration occurs when the molecules spread on the surfaces are close enough to be within the range of each other's attractions and repulsions : when, that is to say, a continuous film is produced. Do the inflection points in the curves in fig. 1 also mark the formation of a continuous sheet ?

The parallelism of the curves for glass and steel shows that the effect which each molecule of the lubricant produces is independent of the nature of the solid surface to which it is applied. The fall in friction due to each molecule is, therefore, a pure function of its field of force, or, in other words, of its atomic configuration.

#### *Solid Lubricants.*

It is more difficult to follow the influence of the quantity of lubricant when it is a solid, because neither primary spreading nor the vapour phase can be made use of.

Surfaces were lubricated with solids either by smearing the lubricant over the plates with a glass rod or by depositing a thin film from solution in ether. A film of insensible thickness was obtained by polishing off as much as possible of the lubricant in the way described below.

In the case of paraffins and alcohols, as the ether evaporates the friction

\* ' Roy. Soc. Proc., A, vol. 85, p. 317 (1913).



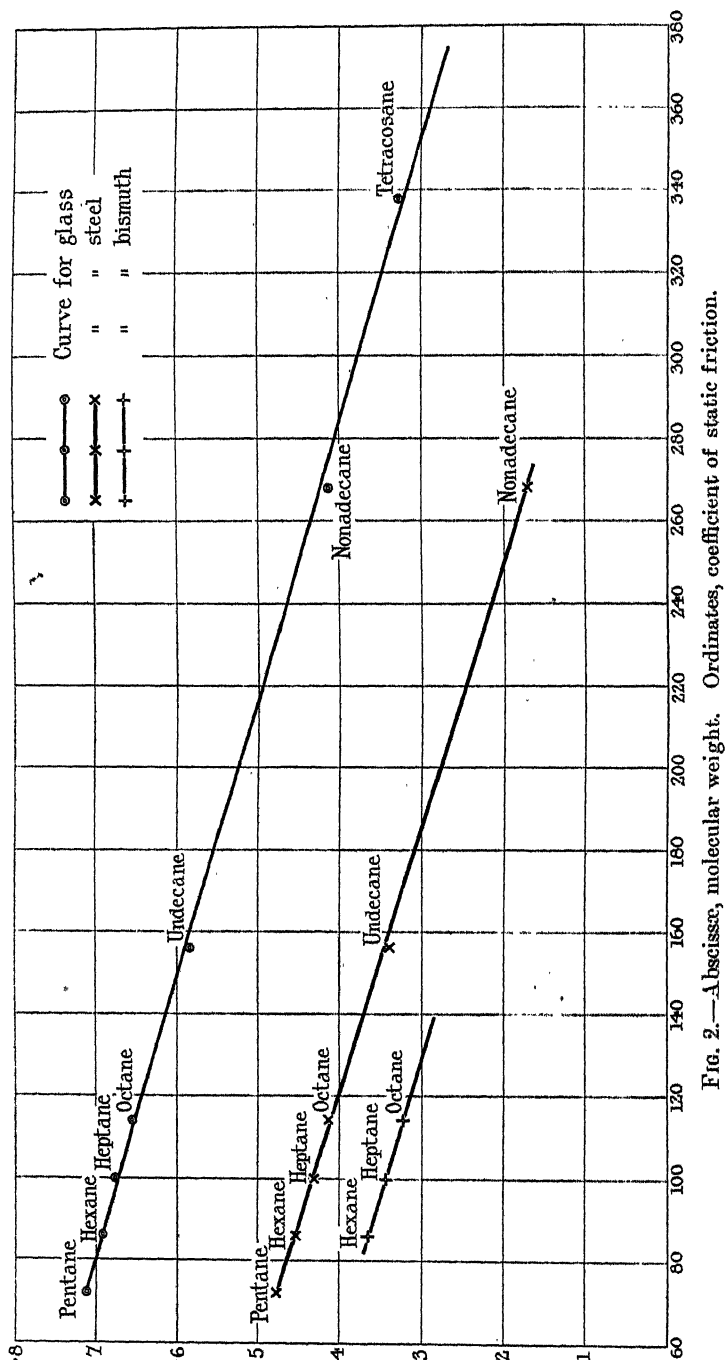


FIG. 2.—Abscisse, molecular weight. Ordinates, coefficient of static friction.

falls until a very low value is reached, which coincides with the presence of the last trace of the solvent. The value persists only for a few seconds, the

friction then rising to a steady value which is that of the pure substance. The final steady values lie on the curve for the series to which the lubricant belongs (figs. 2 and 3). The first set of values shows that for certain mixtures of solvent and solute, in this case ether and the particular paraffin or alcohol, the friction is much less than that obtained when ether is used by itself. The fact that a mixture of two substances may lubricate better than either when used alone was noted in an earlier paper.\* The figures are given in Table V.

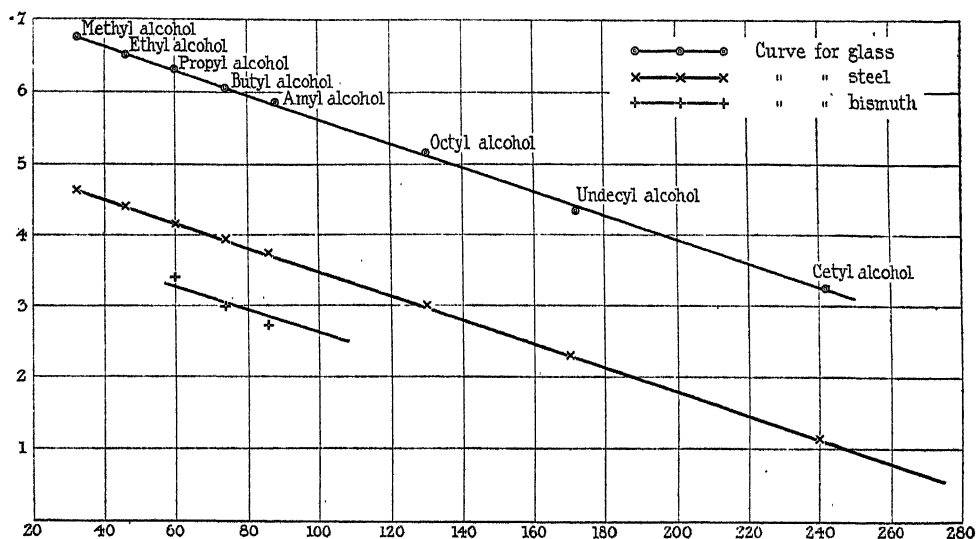


FIG. 3.—Abscissæ, molecular weight. Ordinates, coefficient of static friction.

The solid acids behaved differently. The first two used, namely, decolic acid and dodecoic acid, like the paraffins and alcohols, gave normal steady values for a film deposited from ether (fig. 4), and the polished film gave much lower values, but the higher acids from myristic acid onwards refused to give steady values at all. The explanation is simple. Examination of the surface under the microscope showed that the film of acid was highly crystalline and brittle, so that the slider broke away a crust. The observed friction, therefore, was due mainly to this crust and could be varied merely by moving the slider about on the surface before taking a reading. For example, values from  $\mu = 0.17$  to  $\mu = 0.52$  could be obtained with myristic acid. The crystallisation did not, however, seem to involve the primary film since very thin films deposited from ether were found to give values as low as polished films. Thus, with stearic acid the lowest value ( $\mu = 0.035$ ) obtained was got by depositing a film from an exceedingly dilute solution.

\* 'Phil. Mag.' [6], vol. 40, p. 201 (1920).

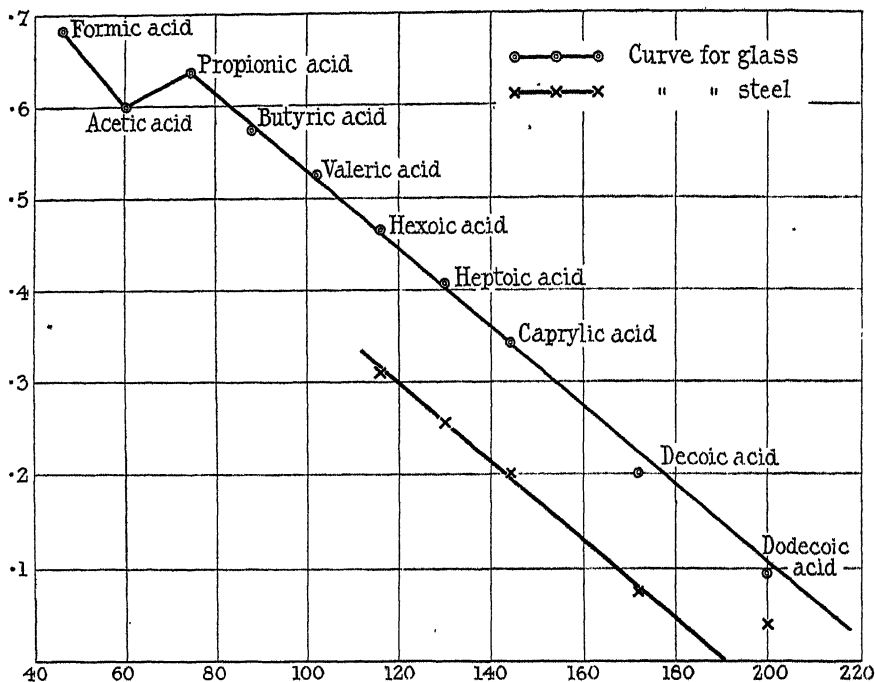


FIG. 4.—Abcissæ, molecular weight. Ordinates, coefficient of static friction.

Table V.—Solid Lubricants.

Lubricant.	Polished film.	Film deposited from ether.	
		Initial value.	Final value.
Glass.			
Undecyl alcohol .....	0·017	0·0781	0·4472
Cetyl alcohol.....	0·019	0·0203	0·3284
Nonadecane .....	0·0467	0·0231	0·4119
Tetracosane .....	0·0321	0·0192	0·3251
Decoic acid .....	0·0632	0·0738	0·2006
Dodecoic acid .....	0·0404	0·0391	0·0983
Myristic „ .....	0·0671	0·0382	Variable results, e.g., myristic acid = 0·24—0·52—0·17—0·31.
Palmitic „ .....	0·0715	0·0340	Palmitic acid = 0·26—0·23—0·37—0·8—etc.
Stearic „ .....	0·0818	0·0296	
Steel			
Nonadecane .....	—	0·0213	0·1783
Cetyl alcohol.....	—	0·0182	0·1126
Palmitic acid.....	—	0·0113	Value irregular.

The increase in the hardness of the crystals with increase in molecular weight probably accounts for the difference in the behaviour of myristic, palmitic and stearic acids, from that of decoic and dodecoic acids.

Attempts were made to polish off both fluid and solid lubricants, with interesting results. For this purpose fragments of fine linen were used which had been exhausted of all "greasy" matter by prolonged extraction with benzene. The linen was regarded as being clean when the friction of a clean surface was not lowered after having been vigorously rubbed with it. In all the operations the linen was not held in the hands but by clean tongs. When the lubricant was a fluid, polishing completely removed it from the surfaces, the friction rising to the clean value, but it was not found possible to polish off a solid lubricant. Polishing a plate covered with a solid lubricant until nothing was visible under a microscope left a surface which gave a very low value for friction. If the normal value of the particular lubricant be that which lies on the curve for its particular chemical series, then polishing produced an abnormally low value. An interesting case is that of undecyl alcohol. This substance melts at 11° C., it was easy, therefore, to apply it either in the fluid or solid states. In the former the alcohol could be completely polished off a surface, whilst in the latter polishing merely served to produce an invisible film having an abnormally low friction. Abnormally low values are also obtained when fluid lubricants are polished, but they are transitory. The figures for polished films appear in Table V.

#### *Influence of Chemical Constitution.*

Table VI gives the coefficient of friction of each substance for glass on glass and steel on steel. The values for bismuth are taken from an earlier paper.

In figs. 2, 3, 4 and 5 these values are plotted against molecular weight. It will be seen that for each chemical series, and for each solid, the curve is a straight line. The equation is, therefore,

$$\mu = b - aM,$$

where  $M$  is molecular weight and  $a$  and  $b$  are parameters. The effect of the nature of the solid face is unexpectedly simple. In changing from glass to steel the curve for a series is merely moved parallel to itself, and in moving from steel to bismuth there is a further shifting. Therefore, in the equation the parameter  $a$  is independent of the nature of the solid face and dependent only on chemical type, varying from one chemical series to another. The parameter  $b$ , on the other hand, is dependent upon the nature of the solid face as well as upon the chemical series.

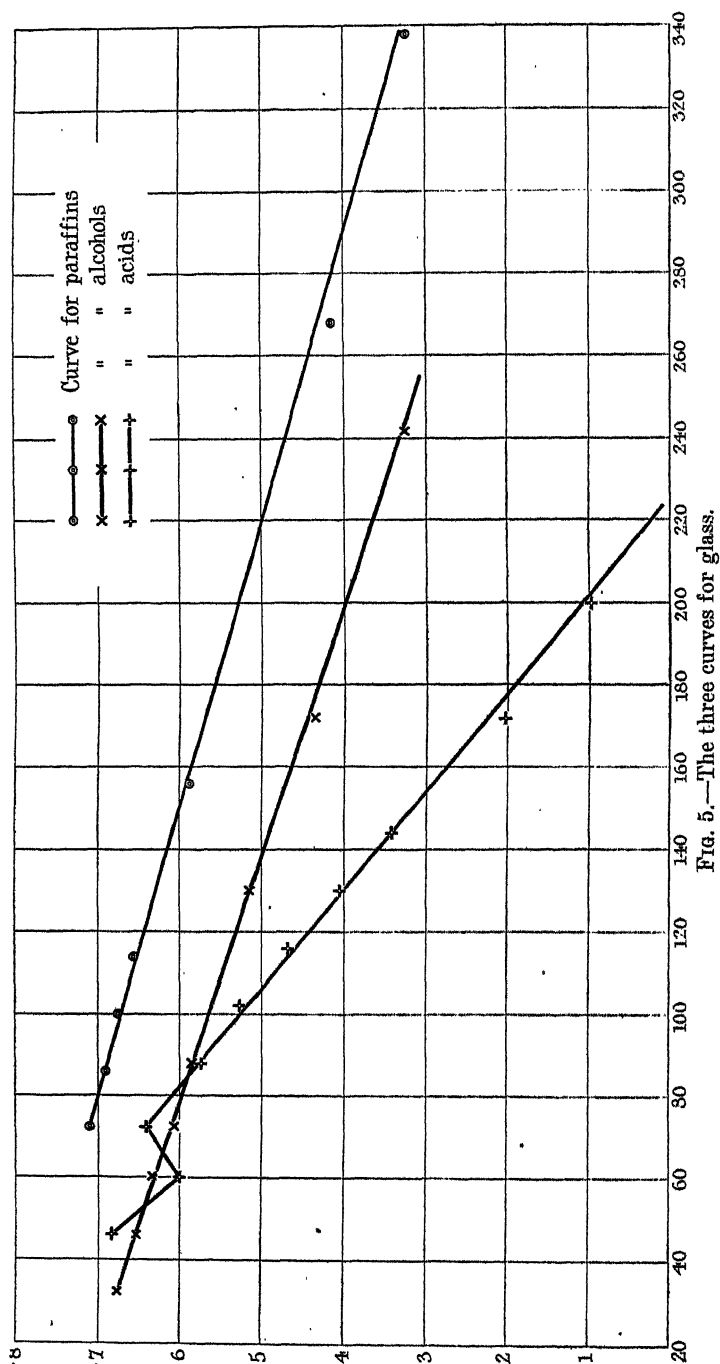


Fig. 5.—The three curves for glass.

Table VI.

Lubricant.	Glass.	Steel.	Bismuth.
<i>n</i> -pentane .....	0·7102	0·4763	—
<i>n</i> -hexane .....	0·6908	0·4528	0·37
<i>n</i> -heptane .....	0·6751	0·4307	0·346
Iso-heptane .....	0·6683	—	—
<i>n</i> -octane .....	0·6552	0·4112	0·32
Undecane .....	0·5908	0·3421	—
Nonadecane (deposited from ether)	0·4119	0·1785	—
Tetracosane (deposited from ether)	0·3251	—	—
Methyl alcohol .....	0·6772	0·4610	0·29
Ethyl " .....	0·6512	0·4408	0·32
Propyl " .....	0·6301	0·4173	0·34
Butyl " .....	0·6061	0·3924	0·30
Iso-butyl " .....	0·6273	—	—
Amyl " .....	0·5854	0·3752	0·27
Octyl " .....	0·5176	0·2981	0·25
Caprylic " .....	0·5373	—	—
Undecylic " .....	0·4455	0·2298	—
Cetyl " .....	0·3253	0·1143	0·17
Formic acid .....	0·6823	—	0·45
Acetic " .....	0·6003	—	0·40
Propionic acid .....	0·6387	—	3·31
Butyric " .....	0·5721	—	—
Valeranic " .....	0·5259	—	0·28
Hexoic " .....	0·4654	0·3108	—
Heptoic " .....	0·4051	0·2556	—
Caprylic " .....	0·3417	0·2003	0·19
Decoic " .....	0·2006	0·0741	—
Dodecoic " .....	0·0983	—	—
Myristic " .....	Readings for smeared faces variable.		
Palmitic " .....			
Stearic " .....			

When other variables are not involved the value of the coefficient of friction is always in the order glass > steel > bismuth. For the two metals this is in the order of their respective hardness. But it does not depend only on hardness, since the steel used was harder than the glass.

The influence of the chemical nature of the solid face is unexpectedly simple in other ways. Thus, for the three lubricants tried; when the slider is of glass and the plate of steel, the value of  $\mu$  is exactly midway between that for glass on glass and steel on steel. The following figures illustrate this:—

Table VII.

Slider.	Plate.	Lubricant.			
		Butyl alcohol.	Amyl alcohol.	Octyl alcohol.	
Glass	Glass	0·606	0·585	0·5176	
Steel	Steel	0·3924	0·375	0·2981	
Glass	Steel	0·493	0·48	0·41	
		} mean 0·4992		} mean 0·4078	
Glass	Glass	0·606	—	0·5176	
Bismuth	Bismuth	0·30	—	0·25	
Bismuth	Glass	0·451	—	0·38	
		} mean 0·453		} mean 0·3838	
Steel	Steel	0·3924	—	0·2981	
Bismuth	Bismuth	0·30	—	0·25	
Bismuth	Steel	0·348	—	0·27	
		} mean 0·3464		} mean 0·274	

To get this simple result the curved surface must be of the softer material. If it be of the harder the figures are different because the softer surface is cut.

#### PART II.—THEORY.

The current view that friction is due to the interlocking of asperities dates back to Coulomb. The asperities of a polished face are no doubt insensible, but earlier writers conceived of them as real elevations of the surface. Herschel, for example, writes: "A surface artificially polished must bear somewhat the same kind of relation to the surface of a liquid, or a crystal, that a ploughed field does to the most delicately polished mirror.\*

Rayleigh† came to the conclusion that the difference between a fluid and a polished surface was not great, the elevations of the latter being of molecular dimensions. Beilby's work on polishing is well known. It confirmed Rayleigh's view.

Coulomb's hypothesis, that friction is due to asperities acting like inclined planes, implies at the limit that the actual surface of the solid is frictionless. This does not seem to be possible, since we know that the surface of a solid is the locus of a powerful field of attraction which is the cause of capillary phenomena, and this attraction, though it may be modified by the film of contamination on all naturally occurring solid faces, is not destroyed by it, otherwise, for example, a drop of water would not cling to a glass rod.

The view taken in earlier papers‡ is that friction is due to molecular attraction operating across an interface, in short, to cohesion. If matter were

\* 'Enc. Met., Art. Light,' 1830, p. 447.

† 'Polish,' Royal Institution, March, 1901.

‡ 'Phil. Mag.' [6], vol. 38, p. 32 (1919); *ibid.*, 49; [6], vol. 40, p. 201 (1920).

continuous, and if the equipotential surfaces of its superficial attraction field were parallel to a plane surface, it would be frictionless. But matter is discontinuous, and it is to this that friction is due. The asperities required by Coulomb are in fact the atoms and molecules, for, owing to the short range of molecular and atomic attractions, the equipotential surfaces are by no means simply parallel to the general material surface. The action of a tangential force does not merely move the atoms and molecules in their own tangent planes, but also rotates them and produces movements of compression along the normal, and the friction—the tangential reaction as French writers call it—is the sum of the resistances to displacements of the centres of mass and to rotation.

When two solid faces are separated by a layer of lubricant the molecules of the latter must be supposed to be highly oriented. The fact that there is a finite resistance to slip shows that the substance of the layer, though it may be formed from material which is fluid at the temperature of observation, has lost its fluidity. This can be due only to the influence of the attraction fields of the solids, which destroys the random arrangement of the molecules which permits of fluidity, and substitutes for it a configuration in which the potential of a molecule is a function of its position and orientation.

The system, therefore, is one which varies rapidly in state along a normal to the solid faces, supposed to be plane, but is homogeneous along surfaces which are parallel to the solid faces. It may be regarded as consisting of a series of imaginary surfaces each having different mechanical properties. When the two solid faces are identical in nature and parallel to each other there may be supposed to be symmetry about a plane surface midway between them, such that surfaces equidistant from this median plane will have identical properties.

When a tangential force is applied there will be "give" at each plane, which will increase with the growth of the applied force until a yield point is reached, when slipping occurs, and, owing to the heterogeneity of state along the normal, the slip is confined to one, or at most two, planes.

The fact that the friction of surfaces flooded with lubricant is the same as that of the same surfaces when covered only with a primary film shows that the layer of lubricant actually present between the opposed faces is identical in thickness and structure in both cases. When the lubricant is in excess this layer will be that which can support the weight of the slider owing to the operation of capillary forces. Let a surface be drawn in the interior of a mass of lubricant resting on a plane solid face at a distance from the solid face equal to the thickness of a primary film. Such a surface must have



peculiar significance in lubrication. It is easy to see why this is so. When a fluid such as, *e.g.*, benzene is poured over a clean surface of water in a vessel, covered so that the space above may become saturated with benzene vapour, it will be noted that, if the sheet of benzene is not too thick, say about 1 mm., it ruptures in places, and contracts to form lenses which are in equilibrium with a composite surface covered with an invisible film of benzene. The continuous sheet of benzene is, therefore, unstable, and it ruptures in the plane which separates the primary film from the mass of the fluid; the benzene below this plane remains adherent to the water, while the benzene above contracts on itself to form lenses or a single lens. The surface mentioned above is, therefore, at that critical distance from the water face at which the attraction of benzene for itself is greater than its attraction for water. It marks what might be called a natural flaw in the structure of the benzene. For this reason it may be expected to be a natural plane of slip when tangential stress is employed, and therefore to be of fundamental importance in lubrication.

Consider two solid faces each covered with a primary film, and let them be applied the one to the other, and let the area of one face be much greater than that of the other. The layer of lubricant may either consist of the two primary films or be greater or less than this, the thickness being determined by the pressure and capillary forces. If it be greater, then the excess must be drawn in between the solid faces by capillary forces from the primary film elsewhere on the surfaces. The balance of probability is that the layer is not thicker than two primary films, for capillary attraction might be expected to draw in more from a flooded face than from a face covered only by a primary film, and the equality in the coefficient of friction proves that this does not happen. Measurements made with sliders loaded excentrically point strongly to the same conclusion (Appendix I). It is not likely to be less than two primary films in thickness, because the coefficient of friction in that case would not equal the flooded value, as the study of the relation to vapour-pressures shows.

The parameter  $\alpha$  measures the contribution of the solid faces to the friction. When two different solids, 1 and 2, are employed the contribution of each, as experiment shows, is  $\frac{1}{2}\alpha_1$  and  $\frac{1}{2}\alpha_2$ , respectively. Therefore each solid face contributes its effect upon the friction independently of the other. The question, however, to which an answer is not readily forthcoming is, Why does the nature of the solid influence the friction of lubricated surfaces at all?

The slipping which occurs when the stress reaches a certain intensity may be due either to a general breakdown of structure in the lubricant or the

structure may persist and the slip be confined to a plane, which is probably the plane midway between the solid faces *when these are composed of the same material*. The fact that there is no break in the curve connecting friction with molecular weight when the lubricant becomes a solid is against there being a general breakdown of structure, for it is unlikely that tangential stress would confer upon a film of a solid lubricant the property of fluidity. A further objection is found in the fact, noted by many writers, that kinetic friction is equal to static friction and is independent of the velocity. This can only mean that static friction measures the maximum tangential stress which a certain molecular structure is capable of bearing. If the structure broke down during relative motion the stress must, we conceive, be changed in amount.

Let us assume, then, that slip is confined to one plane and that the friction measures the tangential reaction at this plane. The reaction depends, as we have seen, not only upon the chemical nature of the lubricant, but also on that of the solids. The field of attraction of the latter must therefore make itself felt in a decisive way at the plane of slip. In the language of the classical theory of capillarity, the range of the force of attraction must be at least equal to half the thickness of the layer of lubricant.

The point at issue will be made clearer by considering this fact in terms of a particular theory of the structure of primary films. When a substance such as, *e.g.*, oleic acid is allowed to spread over water no fall of surface tension is produced until the concentration of the acid on the surface has reached a certain very small value. Rayleigh suggested that this concentration marks the point when the acid forms a continuous layer one molecule thick, when, that is to say, the molecules of the acid are close enough together to be within the range of each other's attraction and repulsion. Increase in concentration of the acid causes the surface tension to fall until a second point is reached, at which further additions cease practically to produce any further effect. The surface is now saturated with the acid and any excess merely collects into lenses of acid in mass. The second point of inflection, therefore, is the point at which the primary film is completely formed. Rayleigh\* suggested that at the second point the layer of acid is two molecules thick.

Rayleigh's first suggestion has been accepted by all who have since worked at the subject. His second suggestion, namely, that the primary film consists of two layers of molecules has not found favour. The view which has replaced it we owe to Devaux,† who considers that the primary film is

\* 'Phil. Mag.' [5], vol. 48, p. 334 (1899).

† 'Rev. Gén. des Sciences,' 4, February, 1913.

always of a single layer of molecules, and that the second point mentioned above occurs when the molecules are packed as closely as possible. The film, in short, is regarded as an elastic structure, which is at its maximal extension when it first begins to affect the surface tension, and at its maximal tangential compression when the surface is saturated. Further compression then results in some of the molecules mounting on top of the layer. This is the monomolecular theory of the structure of these surface films. One of us pointed out that in such films and at all interfaces between immiscible fluids the molecules must be highly oriented with respect to the surface by the asymmetrical field of attraction.

The theory of surface films has been developed on these lines in a striking way by Langmuir\* and Hawkins.† Consider, for example, an acid like palmitic acid. Each molecule consists of a chain of carbon atoms with attached atoms of hydrogen, with a carboxyl group at one end. The carboxyl group is soluble in water, for whereas the paraffins are typically insoluble, the related acids of the lower members of the series are soluble. The carboxyl group may, therefore, be regarded as being much more strongly attracted by water than is the chain of carbon atoms. Langmuir, therefore, pictures a primary film of palmitic acid on water as being composed of molecules attracted to the water by the carboxyl group only, the carbon chain being disposed at right angles to the water surface. The forces of attraction he considers to be of such short range as to extend only from one atom to its immediate neighbours. The influence of the attraction field of the water would, therefore, not extend beyond the atoms of the carboxyl group, the rest of the molecules, consisting of the carbon chain, would be wholly beyond its range. This represents the monomolecular theory pushed to its limits. Imagine the attraction of a solid limited in the same way to the carboxyl group, friction would depend only upon the lubricant and would be independent of the nature of the solid, for cohesion at the plane of slip would then be due only to the terminal group of the chain, namely, the  $\text{CH}_3$  group. We know, on the contrary, that the friction is dependent upon the nature of the solids, and that, therefore, the field of attraction of the solids does not merely serve to anchor the molecules of the lubricant, but must also, in some way, make itself felt at the plane of slip.

One of us has urged that the range of attraction in gases or vapours is quite different from what it is in condensed states of matter. In gases or vapours the range is no doubt very short, so short as to be comparable to the distance between the atoms of a molecule. In fluids, however, there must be

\* 'J. Am. Chem. Soc.,' vol. 39, p. 1848 (1917).

† *Ibid.*

an irradiation of effect. If the field of one atom or molecule tends to orientate the axes of neighbouring atoms or molecules, these in turn will tend to orientate other molecules, and so the effect will spread until, in the case of a fluid, it is finally lost in the heat motions. Such an irradiation of effect must be specially great at interfaces where the general attraction field is itself oriented, and it is this extended range, and not the absolute range of attraction in a vacuum, which is operative in the theory of capillarity. The solids may be supposed to modify cohesion right through a layer of lubricant by spreading of strain in this way, even though the *absolute* range of their attraction may be as small as Langmuir supposes it to be.

The most puzzling questions are, Why should friction fall with increase in the molecular weight of the lubricant, and why should it vary directly with the normal pressure? Coulomb took the fact that friction is independent of the area of the surfaces to prove that it could not be due to cohesion because this obviously varies with the area. Cohesion, he admitted, must play some part, but a small part compared to that due to the "engaging" of asperities. Amontons' law, in that case, would be only an approximation, as Coulomb indeed took it to be. It is, on the contrary, a rigid law, save in those cases in which the traction alters the texture of the solids.

There seems to us to be an unanswerable objection to Coulomb's theory. Let us suppose that the molecules of the lubricant are anchored by the attraction fields of the solid, and that they reduce friction by reducing the inequalities of the solid surfaces. The capacity for reducing inequalities, or filling up depressions, might well be supposed to increase as the molecules got larger, but there are no serious differences in the size of molecules of paraffins and the related acids or alcohols which have the same number of carbon atoms. In other words, the theory fails wholly to explain the connection between chemical constitution and lubrication.

A picture which, however, is purely qualitative, of how molecular weight may influence lubrication is afforded by the assumption that the molecules of the lubricant are oriented by the attraction fields of the solids so that their long axes are at right angles to the solid faces. To give precision to the picture let us assume that the layer of lubricant is composed of two primary films the plane of slip being between them. Each  $\text{CH}_2$  group which is added to the molecule lengthens the carbon chain and, therefore, increases the distance of the plane of slip from the solid faces. But the external tangential force is applied at the solid faces and as the distance is increased the moment of the force at the plane of slip will be increased. Lengthening the carbon chain will, therefore, have an effect similar to the lengthening of a rod when a couple is applied at the ends.

We are, however, no nearer explaining why each carbon atom added to the chain should produce the same effect. If the chain were straight the moment of the tangential force would be proportional to the number of carbon atoms, but it is certain that the chain is either a zigzag or a flat spiral. We are almost driven to the conclusion that in the primary films the atomic pattern of the molecules suffers rearrangement, somewhat like that which occurs in crystal formation. The primary film in a sense may be said to be crystallised, but the pattern is determined by the attraction fields of the solids. The view that a sub-crystalline structure obtains even at interfaces between immiscible fluids was put forward by one of us many years ago. It helps us to understand how the presence of hydroxyl and carboxyl groups may influence lubrication by modifying the attraction field of the solid.

It must be admitted that no explanation of Amontons' law is forthcoming. Like Hooke's law, and the simple linear relation between the concentration of oleic acid on the surface of water and the fall in surface tension, it is probably one of those laws of average values which mask the innate complexity of matter. The most promising way of stating the law is as follows:—For the same solids and the same lubricant the tangential reaction (the friction) per unit area is dependent only upon the pressure. The area now disappears from the equation since it occurs both as numerator and denominator.

An explanation of this relation will be forthcoming only when the theory of boundary friction is developed by some one fully cognisant of the theory of elastic solids. We content ourselves with a suggestion. An equipotential surface drawn above the general plane surface of a solid is not likely to be a plane, because the solid is particulate and each particle is surrounded by a complex field of force. Any equipotential surface is a frictionless surface in the sense that a particle of matter small enough not to distort the surface could be moved over it without effort. In measurements of static friction we can neglect inertia, therefore, if there were no normal pressure due to an external force on the particle, any force having a tangential component would cause it to move over the equipotential surface on which the particle is maintained by attractive and repulsive forces. If there were a normal pressure due to an external force a tangential force would experience resistance to the motion of the particle and the resistance would be proportional to the pressure.

The work done by the external force in the condition of static friction is absorbed by the elastic forces between the atoms and molecules of both lubricant and solid. If the force be applied with sufficient slowness the action is probably thermodynamically reversible, the local cooling or heating effects being reversible. The strain produced by the external force will consist in

displacements of the centres of mass and in rotation of atoms and molecules. When slipping occurs, that is to say in the condition of kinetic friction, we picture the slip as being confined to one plane because the yield point of this plane has been reached. The yield point fixes a limit and therefore (as many observers, from Coulomb onwards, have noted) the tangential reaction of kinetic friction is equal to that of static friction. It follows that the strain during the application of the external force is the same in both states, and the dissipation of energy in kinetic friction is due to the recovery from the strained position of the atoms and molecules which occurs immediately *behind* the slider.

The curves connecting friction and molecular weight, if prolonged, will meet the base line; therefore, when the molecular weight is increased sufficiently static friction vanishes. This point is difficult to observe, for the following reasons. When lubrication is bad the motion which occurs when the slider breaks away is rapid, as though the tangential force necessary to cause the breaking away were in excess of that needed to maintain movement.\* As lubrication is improved the motion takes on more and more the nature of a slow glide, which may be so slight as to be barely detectable. Ricinoleic acid, which is a fluid at ordinary temperatures and a very good lubricant (*cf.* 'Phil. Mag.' 40, 201, 1920), does abolish static friction in the sense that the smallest tangential force which could be applied with our apparatus, namely, that due to the light aluminium pan (= 0.6 grm.), caused the heaviest slider to glide very slowly.

Solid lubricants which should lie on the curve below the base line seem to give finite, but very small, values for static friction. There may, therefore, be a discontinuity between the fluid and solid states in this region. The apparatus, however, was not sufficiently sensitive to settle the point. The values obtained are given below, for what they may be worth:—

Tetracosane on steel .....	$\mu = 0.085$
Dodecoic acid on steel .....	0.031
Dodecoic acid on steel (polished film) ...	0.026
Palmitic acid on steel .....	0.029
Stearic acid on steel .....	0.023

\* This at first sight appears to contradict the equality between kinetic and static friction so often observed, but this equality has been noted in experiments in which both surfaces have had considerable extension. When the surface of the slider is curved and that of the plate plane, motion of the slider tends to cause it to mount on a thickened pad of lubricant.

## APPENDIX I.

Treatises on mechanics deal exclusively with frictionless systems. Painlevé, in 1895, took up the question whether it is possible to develop a general theory for systems with friction analogous, for example, to the application of the equation of Lagrange. His analysis led him to the conclusion that Amontons' law contradicts the equation of motion of a solid, at least in certain realisable cases. This conclusion led to a controversy maintained by French and German writers for about 15 years, which turned on the question whether the condition of absolute rigidity postulated by Painlevé was not responsible for his paradoxical conclusion.

Amongst the many papers is one by Chaumat,\* in which he states that the friction depends not only on the pressure, as Amontons' law states, but also on the degree of asymmetry of the loading. An oval slider, for example, which has a weight placed near one extremity will not conform to the law. In our own experiments the loading was always symmetrical in the case of the steel sliders, which were themselves accurately turned, and any extra weight was added in the shape of circular discs. Loading was not, however, always exactly symmetrical in the case of the glass sliders, since the melted lead with which they were weighted tended to run into an irregular pattern. Measurements were, therefore, made with sliders loaded as unsymmetrically as possible, the weight of lead being either wholly in front or wholly behind the point of application of the external force. In the first case the slider was tilted forward, and in the second case backward by the weights.

The following Table gives flooded values of  $\mu$  for forward-loading, backward-loading and symmetrical loading, in which the external force was applied so as not to cause the slider to rock sensibly :—

Loading.	Lubricant.	
	Octyl alcohol.	Cuprylic acid.
Forward .....	0·5192	0·3423
Backward .....	0·5028	0·3356
Symmetrical.....	0·5176	0·3412

The value for the backward loading is slightly but definitely lower. This, however, does not in our opinion confirm Chaumat's conclusion. Consider a curved slider standing in a pool of lubricant. Chance oscillations tend to bring excess of lubricant between slider and plate in the region of "contact."

\* 'Comptes Rendus,' vol. 136, p. 1634 (1903).

General earth vibrations, due for example to the slamming of a door in the building, were found sometimes completely to upset the readings. A backward-loaded slider was found to be mechanically unstable to vibration. Readings were obtained only by exercising the utmost patience. A backward tilted slider is like a backward tilted plane surface, in that any movement forward due to small vibrations will tend to thicken the layer of lubricant. We conclude, therefore, that the slightly lower value of friction given by backward loading was due to secondary causes.

This is confirmed by the fact that when lubrication was by a primary film, there being no excess of lubricant on the surfaces, the friction was independent of the nature of the loading, as the following values for heptylic alcohol show :—

Forward .....	0.4090
Backward .....	0.4088
Symmetrical .....	0.4050

This result would seem to prove that in lubrication by primary film the slider is not seated on a thickened pad of lubricant drawn in by capillary forces. The layer is indeed composed of a double primary film.

## APPENDIX II.

When a drop of a single pure chemical substance is placed upon a clean surface of water one or both of two things may follow, namely, the spreading from the drop of an invisible film, and the spreading of the drop itself by actual flattening to form a layer which, at any rate at first, is of sensible thickness. These processes are distinct, because the first may occur without the second. Spreading of the drop itself occurs only when the surface tension of water is greater than the sum of the tensions of the upper and lower surfaces of the drop. It is this kind of spreading which is contemplated in the classical theory of capillarity. Normal paraffins with more than eight carbon atoms, and stable saturated substances like carbon tetrachloride, do not manifest this kind of spreading; but, if they have a sensible vapour pressure, an invisible film is formed, not directly from the drop, but through the mediation of the vapour phase. The formation of the insensible film is called primary spreading, whilst the flattening out of the drop is called secondary spreading.\*

There can be no manner of doubt but that primary spreading on solid faces occurs through the intervention of the vapour. Only those lower members of a series which have a sensible vapour pressure manifest it, and, as the

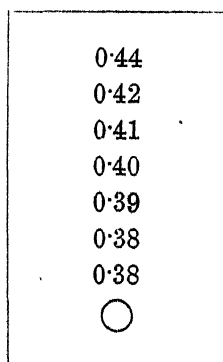
\* 'Roy. Soc. Proc.,' A, vol. 88, p. 313 (1913); 'Phil. Mag.,' vol. 38, p. 49 (1914).



molecular weight increases, and the vapour pressure decreases, the film forms more and more slowly. The time taken, after the drop was in position, for the friction to become uniform all over the plate at the critical or "flooded" value was, in minutes:—

Lubricant.	Glass.	Steel.
Methyl alcohol.....	5	—
Ethyl " .....	5	—
Propyl " .....	10	—
Butyl " .....	20	20
Octyl " .....	35	40
Acetic acid .....	5	—
Butyric acid .....	10	—
Heptylic " .....	40	—
Caprylic " .....	50	45
Undecane .....	5	5

The gradual formation of the film is shown by the following diagram, in which the position of the drop of butyl alcohol on the steel plate is indicated by a circle, and the figures give the value of the coefficient of friction at the place where they are printed, ten minutes after the drop was placed on the plate.



*The Influence of Temperature on Two Alternative Modes of  
Decomposition of Formic Acid.*

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It is generally agreed that the very rapid increase with temperature of the velocity of chemical change is only to be explained by the assumption that the reactive molecules are those of relatively large internal energy-content. Whether the activation of molecules is brought about by collisions with other molecules, or by the absorption of quanta of radiation, is at present a matter of controversy. But, given that activated molecules are produced in one of these ways, the further question arises as to whether every molecule with the necessary critical energy reacts at once, or whether in addition to possessing this it must be in a certain phase. In the first case the velocity of a chemical change would be simply governed by a "time of relaxation" in the sense of the kinetic theory, while in the second case an additional specific factor would be concerned.

Investigations have failed hitherto to give an unequivocal answer to this question, but the study of the influence of temperature on two simultaneous modes of decomposition of a molecule such as formic acid appeared to offer an opportunity of deciding it.

If  $E_1$  and  $E_2$  are the critical energies for the two alternative reactions and  $N$  the total number of molecules, it follows from the kinetic theory that the numbers of molecules possessing these respective energies are

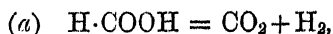
$$N_1 = N e^{-E_1/RT} \text{ and } N_2 = N e^{-E_2/RT},$$

taking a system of two degrees of freedom for mathematical simplicity. Then  $\frac{N_1}{N_2} = e^{-(E_1-E_2)/RT}$ , so that if one mode of reaction is associated with a slightly lower critical energy it would predominate very largely if the number of active molecules were the only factor.

Actually we find that, although two alternative modes of decomposition of formic acid proceed with the same order of velocity, yet the critical increments are so different that one reaction should predominate almost entirely unless a phase restriction is introduced, and we suggest a possible interpretation of the phase factor in this specific instance.

The thermal decomposition of formic acid is subject to a variety of catalytic

influences which govern not only the velocity of the decomposition but also the nature of the products. Sabatier and Mailhe\* have shown that the acid may break up in the following ways:—



Of these reactions only (a) and (b) are of importance under the conditions of the experiments to be described. The approximate position of equilibrium in each can be calculated by Nernst's theorem, but there is some uncertainty both as to the heats of reaction and the chemical constant of formic acid. Assuming Thomsen's value of 69,400 calories for the heat of combustion of formic acid, reaction (a) is accompanied by the development of 1,000 calories and reaction (b) by the absorption of 9,100 calories. Taking the chemical constant of formic acid as 3.3 (Pollitzer) and considering formic acid vapour as unassociated,† the following equilibrium constants have been calculated:—

Temperature.	(a). $\frac{[\text{HCOOH}]}{[\text{CO}_2][\text{H}_2]}$	(b). $\frac{[\text{HCOOH}]}{[\text{CO}][\text{H}_2\text{O}]}$	$\frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$	
			Ratio (a)/(b).	Haber calc.
200° C.	$2.27 \times 10^{-7}$	$5.33 \times 10^{-5}$	$4.26 \times 10^{-3}$	$3.5 \times 10^{-3}$
300° C.	$1.96 \times 10^{-6}$	$6.97 \times 10^{-6}$	$2.8 \times 10^{-2}$	$2.1 \times 10^{-2}$

It is, therefore, clear that the formic acid is almost completely decomposed in the equilibrium mixture. As a check on the calculations the value of the equilibrium constant of the water gas reaction obtained as the ratio of the equilibrium constants for (a) and (b) is compared with the constant calculated from Haber's equation.‡ The agreement is satisfactory.

We have determined the velocity of decomposition of formic acid in glass vessels between 240° and 300° C. when reactions (a) and (b) proceed simultaneously. Both reactions appear to take place on the surface of the glass, and they follow the monomolecular law, but the chief interest of the work lies in the fact that their temperature coefficients differ considerably.

The method of experiment consisted in measuring the increase in pressure which accompanies the decomposition of formic acid vapour, and in analysing.

\* 'C. R.,' vol. 152, p. 1212 (1911).

† Peterson and Ekstrand found only 5 per cent. association at 214° C.

‡ 'Zeit. Phys. Chem.,' 1910, vol. 68, p. 731.

the gaseous products of decomposition in a Haldane gas-analysis apparatus. The decomposition vessel consisted of a cylindrical bulb, of about 8 c.c. capacity, drawn out at the upper end for the purpose of filling, the lower portion being sealed to a capillary mercury manometer. The cross-section of the latter was sufficiently small to enable the change in volume of the vapour in the bulb due to the rise of the mercury in the capillary to be ignored. The bulb was filled with formic acid vapour as in the Dumas method of determining vapour densities. Transfer of the gas to the Haldane apparatus was effected by a piece of rubber tubing filled with mercury under which the tip of the bulb was broken. The proportions of carbon monoxide, carbon dioxide and hydrogen were determined in each reaction product. Vapour baths of boiling quinoline and other liquids were used as thermostats.

The decomposition always follows the monomolecular law as illustrated by the following example:—

Decomposition of 85 per cent. Formic Acid at 283° C.

Time in minutes. <i>t</i> .	Increase of pressure in mm. of Hg. <i>x</i> .	$k = 1/t \log_e 475/475-x$ .
11	73	0·0152
24	149	0·0157
36	203	0·0154
50	251	0·0150
75	318	0·0148
105	383	0·0156
128	416	0·0163
∞	475	—

Similar results were obtained with 96 per cent. acid, showing that the presence of some water initially does not affect the reaction appreciably. The relative velocities of reactions (a) and (b) vary considerably with the nature of the glass surface, and may differ even in two bulbs made of similar glass and of the same area and volume, so that in order to determine their temperature coefficients series of measurements were made at different temperatures in the same bulbs with the following results ( $k_{CO_2}$  and  $k_{CO}$  being the velocity constants for reactions (a) and (b) respectively):—

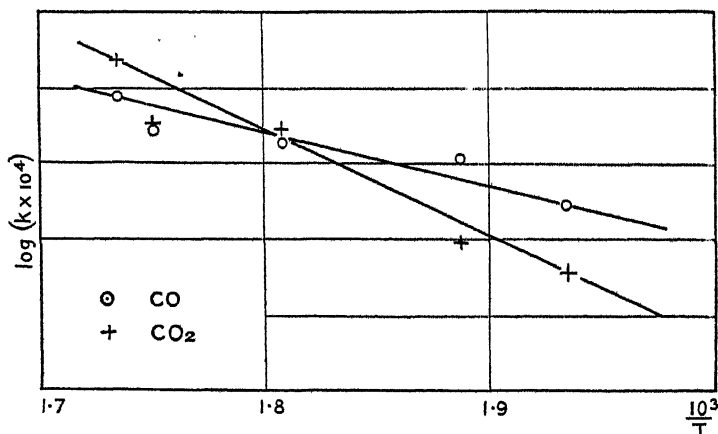
	Temperature.	$k_{\text{total}}$ .	$k_{\text{CO}_2}$ .	$k_{\text{CO}}$ .	Ratio $k_{\text{CO}_2}/k_{\text{CO}}$ .
Bulb 1 .....	°				
	244	0·0023	0·00061	0·0017	0·35
	257·5	0·0045	0·00099	0·0035	0·28
	280	0·0095	0·0051	0·0044	1·16
	298	0·0107	0·0056	0·0051	1·10
	303	0·0237	0·0152	0·0085	1·7
Bulb 2 .....	244	0·00147	0·0057	0·00090	0·63
	302	0·0160	0·0117	0·0043	2·70
Bulb 3 .....	244	0·00084	0·00015	0·00069	0·21
	300	0·0145	0·0086	0·0059	1·5
Bulb 4 .....	244	0·00108	0·00028	0·00080	0·35
Bulb 5 .....	243	0·00057	—	—	—

Values for similar bulbs at 244° containing varying amounts of broken glass or quill tubing were as follows:—

$k_{\text{total}}$ .	$k_{\text{CO}_2}$ .	$k_{\text{CO}}$ .	$k_{\text{CO}_2}/k_{\text{CO}}$ .
0·0167	0·0016	0·0095	0·17
0·0044	0·00088	0·0035	0·25
0·0025	0·00045	0·0020	0·23
			0·22

The mean value of  $k_{\text{total}}$  for bulbs without added glass was 0·0012 at 244°.

The results obtained with bulb 1 are plotted in the diagram. The



following temperature coefficients for a rise of 10° C. have been calculated by plotting  $\log k_{\text{CO}_2}$  and  $\log k_{\text{CO}}$  against temperature for each series of experiments:—

Ratio for Rise of  $10^\circ$  ( $k_{t+10}/k_t$ ).

	$k_{\text{CO}_2}$	$k_{\text{CO}}$
Bulb 1.....	1.74	1.29
Bulb 2.....	1.68	1.31
Bulb 3.....	2.06	1.47
Mean .....	1.83	1.35

Thus, although the values of the velocity constants in different experiments at the same temperature differ considerably owing to the varying catalytic properties of the surface, it is clear that reaction (a) producing carbon dioxide has a much higher temperature coefficient than reaction (b) producing carbon monoxide.

The following points, however, require consideration before any special significance is attached to this result:—

1. As, according to Haber's results (*loc. cit.*), the proportion of carbon dioxide to monoxide in the equilibrium water gas mixtures would be 6.9 at  $300^\circ\text{C}$ . and 3.7 at  $400^\circ\text{C}$ ., the increased proportion of carbon dioxide formed at the higher temperatures might be due to the secondary interaction of carbon monoxide and water vapour if the water gas equilibrium is established sufficiently rapidly in glass vessels at  $300^\circ$ . This point was tested experimentally, and it was found that the rate of this secondary reaction was negligible even at  $350^\circ$ .

2. In order to prove that the formation of carbon dioxide was not favoured by the higher vapour pressure of mercury at the higher temperature, a series of experiments were made in sealed glass bulbs without a mercury manometer. The analysis of the gaseous products showed that the proportion of carbon dioxide and hydrogen increased at higher temperatures as in the presence of mercury. The results are tabulated below, and incidentally they illustrate the curious influence of the nature of the glass on the course of the decomposition:—

Bulb.	Glass.	Ratio $\text{CO}_2/\text{CO} + \text{CO}_2$ .		
		$349^\circ$ .	$302^\circ$ .	$239^\circ$ .
1	Soda .....	0.90	0.74	0.39
2	Soda .....	0.76	0.73	0.48
3	Soda .....	0.84		
4	Jena .....	0.86	0.68	0.63
5	Jena .....	0.90		
6	Borosilicate .....	0.89		
7	Borosilicate .....	0.92	0.85	0.76

In the Jena glass there was always less hydrogen produced than carbon dioxide, indicating that reaction (c) had taken place to a small extent. This agrees with the observations of Sabatier and Mailhe.

3. Finally, it was necessary to consider the possibility that the high temperature coefficient of the reaction  $\text{H.COOH} = \text{CO}_2 + \text{H}_2$  might be due to its taking place to a considerable extent in the homogeneous phase at the higher temperatures. The relation between the velocity of decomposition and the area of the surface of the glass exposed was therefore investigated at  $294^\circ \text{C}$ . in the following way:—

Two pairs of bulbs were blown, the two bulbs of each pair being of glass cut from the same length of tubing, in order that the nature of the surface might be the same in each case. Into one bulb of each pair were placed fragments of glass (about 1 square cm. in area), prepared by breaking up a measured cylinder of the same glass as the corresponding bulb. In this way two pairs of decomposition vessels were made, the bulbs of each pair being of the same glass, but differing in area and volume.

If the reaction at this higher temperature ( $294^\circ \text{C}$ .) takes place to any considerable extent in the homogeneous phase, the velocity should be much less dependent upon the ratio area/volume than at lower temperatures. Actually, it is found that the velocity of reaction increases not merely in proportion to the area of the walls of the vessel, but even more rapidly, since, apparently, the sharp edges of the pieces of glass added are specially active. The results obtained were:—

$$\text{First pair of bulbs, } a \text{ and } b \quad \frac{(\text{area/volume})_a}{(\text{area/volume})_b} = 3.6.$$

$$\frac{k_{\text{CO for } a}}{k_{\text{CO for } b}} = 8.1, \quad \frac{k_{\text{CO}_2 \text{ for } a}}{k_{\text{CO}_2 \text{ for } b}} = 7.8.$$

$$\text{Second pair of bulbs, } c \text{ and } d \quad \frac{(\text{area/volume})_c}{(\text{area/volume})_d} = 3.1.$$

$$\frac{k_{\text{CO for } c}}{k_{\text{CO for } d}} = 4.0, \quad \frac{k_{\text{CO}_2 \text{ for } c}}{k_{\text{CO}_2 \text{ for } d}} = 6.3.$$

From this it is clear that, even at  $294^\circ$ , the carbon dioxide reaction is still as largely influenced by the surface of the glass as the carbon monoxide reaction.

It appears, therefore, that the heterogeneous reactions involved in these two modes of decomposition of formic acid really have very different temperature coefficients, and that one of them is of the same order as that characteristic of a homogeneous reaction. This obviously lends support to the theory of heterogeneous catalysis, which assumes the reaction to take place slowly in a unimolecular layer at the surface of the catalyst, rather

than to the old theory, which assumes the reaction to take place rapidly on the surface of the catalyst, its velocity being determined by the rate of diffusion through an absorbed layer of considerable thickness. In the case investigated, both reactions would be affected equally by the rate of diffusion of the formic acid.

Calculating the critical increments for the two reactions from the formula  $\frac{d \log k}{dT} = \frac{E}{RT^2}$  we find for the decomposition giving the monoxide  $E_{CO} = 16,000$  calories per molecule (approx.), and, for the dioxide,  $E_{CO_2} = 28,000$  calories (approx.). (An assumption underlies this procedure, namely, that the extent of the glass surface covered does not vary with temperature. This can only be approximately true, but, since the reactant is the same in each reaction, the relative value of the two critical energies will not be seriously in error.)

Since the numbers of molecules activated for the two reactions are proportional to  $e^{-28000/RT}$  and  $e^{-16000/RT}$  about  $e^{10}$  molecules should yield carbon monoxide for one yielding the dioxide. Actually, the rates are of the same order. Hence the idea of a phase restriction.

The following suggestion is only intended to illustrate how the phase condition may be interpreted physically. Suppose the formic acid molecule adsorbed on the surface by the residual affinity of the  $>CO$  group. In the case of a sufficiently activated molecule, a violent collision between the  $-H$  and  $-OH$  groups may occur, and a hydrogen molecule be split off. Although the requisite degree of activation may be attained but rarely, nevertheless, a high percentage of these collisions in the activated molecules may result in this type of decomposition. On the other hand, for water to be eliminated and carbon monoxide left, a high degree of activation is not required, possibly as the removal of an  $-OH$  group, as a whole, from an organic compound is a much less profound change than the fission of the hydrogen and oxygen, but very few of the activated molecules may decompose because it is necessary to await the contingency that the forces holding the  $-OH$  and  $-H$  to the carbon should be in a weak enough condition simultaneously to allow "uncoupling" of the molecule.

We are well aware that this is an *ad hoc* hypothesis, but it appeared better to attempt a physical interpretation than to leave the phase-factor as a purely mathematical conception.

We wish to express our thanks to Dr. C. G. Douglas, who kindly lent the Haldane apparatus with which the analyses were made.



*Researches on the Chemistry of Coal. Part II.—The Resinic Constituents and Coking Propensities of Coals.*

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*Introduction.*

This paper embodies the results of experimental investigations, carried out during the past five years in the Fuel Laboratories of the Imperial College of Science and Technology, South Kensington, into the resinic constituents of bituminous coals and their supposed determining influence upon the coking propensities thereof.

The property of "coking," when carbonised at 900°–1000° C., is not inherent in all "black" coals, but varies from zero up to a high degree. Although, to some extent, it appears to be connected with the amount of volatile matter yielded by the dry ashless coal substance at such temperatures, the connection is by no means so direct as is sometimes supposed. Thus, whilst it may be said to be generally non-existent in coals yielding below 15 or above 45 per cent. of "volatiles," and to be at its maximum in those yielding between 15 and 30 per cent., and whereas also it gradually diminishes as the yield of "volatiles" rises above 30 per cent., yet there is no corresponding gradual diminution as the yield falls below 20 per cent. Indeed, in the region of 15–20 per cent. of "volatiles" there is an abrupt failure of coking properties; for in this region—and particularly at about 15 per cent.—are to be found not only some exceptionally strongly-coking coals, but also many that are quite devoid of the property. The reason for such an apparently sudden disappearance of coking properties in the said region remains one of the unsolved questions in the chemistry of coal.\*

The attention of one of us was recently drawn to a striking instance of this kind whilst engaged upon an investigation of certain Spanish coals, which from our point of view proved to be of exceptional interest. They were representative samples, each taken from a series of three adjacent seams (called Nos. IV, V and VII respectively) of carboniferous age

\* We do not say that there is any definite point in the volatile-yield at which the coking properties suddenly fail, because there is an "overlap" between coking and non-coking coals in the range between 15 and 20 per cent.; what we rather mean is, that while with diminishing volatiles below 20 per cent. the coking properties disappear, they do so abruptly, and not gradually as they do with increasing volatiles above 30 per cent.

occurring in a range of hills running roughly E. and W. near the towns of Ponferrada and Villablino in the Province of Leon (N. Spain). The three seams in question are separated from each other by distances varying between 10 and 20 metres; and 100-lb. samples had been carefully taken from each of them under proper supervision from a fresh coal surface in the mine. No. IV was from a seam (0·6–1 metre thick), of hard-coking coal; No. V was from the next seam (varying up to 2 metres thick) of a moderately good coking coal; whilst No. VII was from a third seam (0·5 metre thick) of a semi-bituminous (or perhaps anthracitic) type quite devoid of coking properties. The ultimate compositions of the dry ashless coal substances in each case are given in Table II (Coals C, D and E), (*q.v.*); the amounts of "volatiles" at 900° C., yielded by the dry ashless coal-substances in each case, were as follows:—

Table I.

Seam.	No. IV. Hard-coking.	No. V. Coking.	No. VII. Non-coking.
Per cent. "volatiles" 900° C. ....	21·70	22·65	17·80

The abrupt change from the well-marked coking quality of No. V to the absolutely non-coking character of No. VII in two neighbouring seams is a most interesting example of how two coals of very similar carbon, hydrogen, and oxygen contents (*vide* Table III), can yet differ absolutely as regards their coking qualities. That the change in question may possibly have been due to some igneous intrusion in or near seam No. VII, subsequent to the formation of the seams, is suggested by the occurrence of porphyritic rock in the roof of same, and also by the lower volatile yield of the coal substance on being carbonised at 900° C., as compared with the corresponding yields for the coals from the neighbouring coking seams. Some experiments with these coals were included in this research.

In this connection also mention may be made of some suggestive observations made during another investigation recently carried out at the Imperial College by one of us in conjunction with Mr. J. Roberts upon the coking properties of certain South Wales coals from seams that were "faulted" in places. In many such instances it was found that samples taken at or near the "faulted" part of a seam yielded decidedly less volatile matter, and sometimes also a denser coke, than those taken from the "unfaulted" part of the same seam, as though the coal had been partly carbonised *in situ* in the locality of the fault. In one case, such a "faulted"

coal yielded 18·9 per cent. of volatiles at 900° C., as against 23·4 per cent. yielded by the normal coal from the unfaulted part of the seam. Thus the abnormal conditions of pressure and temperature, which must have prevailed locally when the "faulting" occurred, were sufficient to diminish materially the volatile contents of the coal in the region of the fault, and, at the same time, to alter its coking properties.

Some authorities have connected the coking propensities of coals with the presence in them of resinous constituents. Many years ago Carrick Anderson, in an important memoir upon the coking properties of certain Scottish coals,\* ascribed them mainly, if not exclusively, to the presence of bodies of a resinoid character which are capable of extraction with dilute caustic potash solution. Later on, Bedson† found that the coking properties of a coal are destroyed when it is extracted with pyridine; such procedure, however, besides removing resins, also depolymerises the main coal-substances.

In 1913 Clark and Wheeler, by subsequently treating such pyridine extracts with chloroform, claimed to have effected "a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated,"‡ and they considered that the "binding principle" of coking coals lies chiefly in the chloroform soluble portion of their pyridine extracts, which they described as "resinic" in character. In the light of our results, however, this conclusion needs modification.

About a year ago S. R. Illingworth,§ in publishing some researches upon South Wales coals, put forward the "resinic coking theory" in a rather extreme and, as it seems to us, untenable form. He concluded that the plasticity of coking coals is due to the liquation of their resinic constituents by heat, and that, in general, 5·5 per cent. is the minimum amount of resinic matter necessary in a coal for the formation of coke and to render a coal mass plastic when heated.

The results of our researches, however, seem definitely opposed to the theory that the resinic constituents of a bituminous coal are the sole, or even the main, cause of its coking properties, although they may be a contributing factor.

\* 'Journ. Soc. Chem. Ind.,' 1898, p. 1017.

† 'Journ. Soc. Chem. Ind.,' 1908, p. 147.

‡ 'Journ. Chem. Soc.,' vol. 103, p. 1706 (1913).

§ 'Journ. Soc. Chem. Ind.,' vol. 39, pp. 111 and 134 (1920).

# EXPERIMENTAL PART.

## A. Character of the Coals Investigated.

Eight different coals (designated as A, B, ... G, H), in which the coking propensities varied from zero to a very high value, were selected for the investigation. Of these, the first two (A and B) were, respectively, the Durham coking coal and the Barnsley hard steam coal employed by Bone and Sarjant in Part I hereof.\* The next three (C, D and E) were selected from the interesting series of Spanish coals already referred to, C being strongly-coking, D moderately so and E absolutely non-coking. F and G were South Wales coals; F giving a very hard and dense metallurgical coke, and G being a non-coking anthracitic variety. H was a homogeneous vitreous "jet-like" coal found in a thin bed in the Oolitic ironstone deposits of the Cleveland district of N. Yorkshire.

Incidentally also, some experiments were made upon a Nigerian black coal, which on carbonisation at 900° C. yielded a slightly coherent residue, and 45 per cent. of volatiles referred to the dry ashless coal-substance. The ultimate compositions, both of the dry coals A to H inclusive, and of their dry ashless substances, are given in Tables II and III which also record

Table II.—Ultimate Composition of the Dry Coals Investigated.

	A. Durham coking.	B. Barnsley.	C. Spanish.	D. Spanish.	E. Spanish.	F. South Wales.	G. South Wales.	H. Oolitic.
Carbon .....	82·73	82·33	78·30	74·25	82·80	82·58	86·80	75·32
Hydrogen .....	4·76	4·99	4·30	4·02	4·15	4·56	3·82	6·31
Nitrogen .....	1·09	1·50	1·40	1·09	1·93	0·94	0·38	0·97
Sulphur .....	1·28	0·70	0·75	1·35	0·72	0·47	0·96	0·67
Oxygen* .....	7·38	7·72	6·00	3·04	3·85	7·59	5·52	6·72
Ash .....	2·76	2·76	9·25	16·25	6·55	3·86	2·52	10·01
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Character of coke	Hard	Moder- ately hard	Very dense and hard	Hard	Nil	Very dense and hard	Nil	Light porous.
Volatile matter expelled at 900° C.	26·3	32·2	19·6	19·0	16·75	21·7	9·9	53·8

\* As is usual in stating the results of coal analyses, the oxygen has been estimated "by difference."

\* 'Roy. Soc. Proc.,' A, vol. 96, p. 119.

Table III.—Ultimate Composition of the Dry Ashless Coal-substance.

	A.	B.	C.	D.	E.	F.	G.	H.
Carbon .....	85·07	84·68	86·28	88·65	88·59	85·90	89·04	88·70
Hydrogen .....	4·90	5·13	4·74	4·80	4·44	4·74	3·92	7·01
Nitrogen .....	1·12	1·54	1·54	1·30	2·07	0·98	0·39	1·08
Sulphur .....	1·32	0·72	0·83	1·61	0·77	0·40	0·98	0·74
Oxygen* .....	7·59	7·93	6·61	3·64	4·13	7·89	5·07	7·47
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Volatile matter expelled at 900° C.	27·0	33·1	21·7	22·7	17·9	22·6	10·2	59·8

\* As is usual in stating the results of coal analyses, the oxygen has been estimated "by difference."

the yields of volatile matter at 900° C. and the coking properties in each case. With regard to the latter, it may be said that coals C and F (Spanish and Welsh respectively) yielded the densest and hardest cokes of all. A represents the celebrated Durham coking coals which are employed for manufacturing the metallurgical coke used in the Cleveland blast-furnaces; D (Spanish) and B (Barnsley) gave fairly strong cokes; H (Cleveland Oolitic) gave a very light and porous coke; whilst E (Spanish) and G (South Wales anthracitic) were quite devoid of coking properties.

#### *B. Effect on the Coking Properties of Extracting Coals with Various Resin-solvents.*

It was decided first of all to investigate the effect on the coking properties of bituminous coals of a thorough extraction with resin-solvents such as ethyl ether, acetone, ethyl alcohol, chloroform, benzene and xylene.

Atmospheric oxidation is known to affect the coking power of coal; and as Bone and Sarjant (*loc. cit.*) have also shown that it may seriously influence the action of solvents on the coal substance, it was necessary to carry out the extractions in an atmosphere of nitrogen. For this purpose the following special form of Soxhlet apparatus was designed, as an improvement upon that previously described by Bone and Sarjant.\*

The flask F of about 450 c.c. capacity, was sealed to a wide tube, T, of 4·5 cm. internal diameter. In this tube was placed the syphoning-cup, S, which was supported by the constriction at N, and measured 10 cm. in depth by 3·3 cm. diameter. A small hole in the upper edge of the cup facilitated

\* *Ibid.*, pp. 123-127.

the lifting of it out, when necessary, by means of a hooked wire. The upper end of the wide tube, T, carried, on a ground joint, the internal water-cooled condenser, C. It was expanded a little above the joint so as to form a mercury seal, and the expansion was drawn out to a spout on one side. The effective part of the condenser was 12 cm. long by 3 cm. diameter. Just below the condenser-joint was a side tube, which was connected to a tap, R, and also to a vertical capillary tube, M, which dipped into a mercury seal, K. The connection was made either by rubber tubing or a ground glass joint.

The advantages of such an apparatus are:—

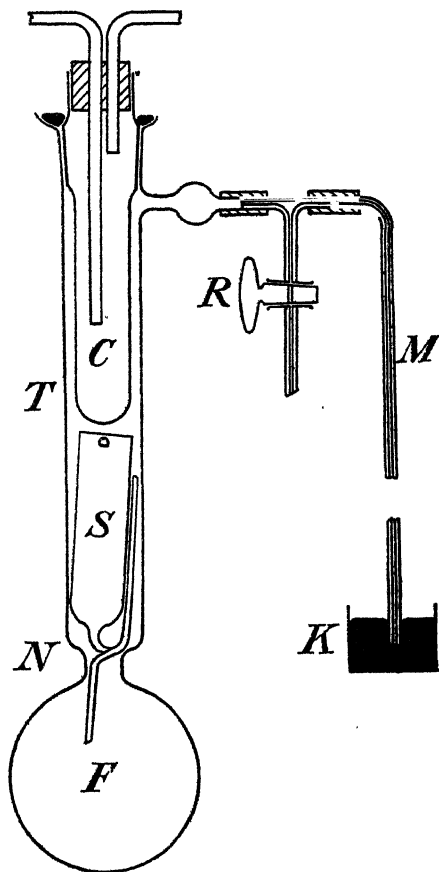
(i) Extractions can be carried out in any desired atmosphere.

(ii) By partially evacuating the apparatus, the temperature at which extraction is carried out can, if desired, be reduced below the boiling-point of the solvent at normal pressure; this is an advantage when the substance under treatment is of an unstable nature.

(iii) Loss of the solvent is almost impossible, because its vapour is condensed before it can reach the joint or side-outlet above. For the same reason there is no risk of the extracted matter being contaminated by grease or other substance used to lute the said joint.

(iv) The insoluble residue after extraction may easily be dried without exposing it to atmospheric oxidation; for this purpose the syphoning cup is removed from the apparatus, suitably stoppered, and warmed while a current of inert gas is passed through it by way of the tail-tube.

In the first instance two series of experiments were carried out with seven of the coals, namely, A, B, C, E, F, G, and H. Dried samples of these, ground so as to pass through a mesh of 90 to the linear inch, were extracted with (a) acetone (b.p. 56.5°) and (b) benzene (b.p. 80.4°) respectively for a



continuous period—in each case, of from 7 to 13 days—until no appreciable further extraction took place. The percentage amounts of extract (referred to the dry coal) are shown below :—

Table IV.—Results of Soxhlet Extraction of Coals.

Coal.	A.	B.	C.	E.	F.	G.	H.*
Solvent—							
Acetone .....	2·38	2·66	1·40	0·66	0·67	0·68	9·95 per cent. extracted.
Benzene .....	3·27	1·86	2·04	1·25	1·18	0·98	

\* In the case of this coal, the acetone-extraction was not completed in 11 days; on continuing the process for altogether 36 days 12·56 per cent. of the coal was extracted without impairing its coking properties.

So far as could be judged, the coking propensities of the five coking coals, A, B, C, F, and H, were unimpaired by the treatment; the same applied to the strongly-coking Spanish coal, C, even after it had been similarly extracted with xylene (b.p., 142°), for a period of 3 days, during which it gave 2·58 per cent. of soluble extract.

Seeing that the solvents employed in the foregoing experiments would almost certainly remove the greater part, if not all, of any free resin disseminated through the coal-substance, these results seemed to cast doubt upon the commonly accepted theory that the coking power of coals depends on their resinous constituents. In order, however, that there might be no doubt about the matter, it was decided to extract the two hard coking coals, A and B, *successively* with (a) ethyl ether (11 days), (b) ethyl alcohol (9 days), and (c) benzene (15 days). The results of these further experiments are given below :—

Table V.—Prolonged Soxhlet Extraction of Coals A and B, with three Resin Solvents in Succession.

Coal.	A.	B.
Ethyl ether (11 days) .....	2·20	2·34 per cent. extracted. 1·88   "   " 0·89   "   "
Ethyl alcohol (9 days) .....	2·48	
Benzene (15 days) .....	2·00	
Total .....	6·68	5·11

In view of the fact that the resins which are known to occur macroscopically in carboniferous coal seams\* are similar in solubility to contemporary

\* *Vide* W. A. Bone, 'Coal and its Scientific Uses,' pp. 78-80.

resins, it seems probable that so drastic an extraction, employing successively the three solvents named, would remove all free resins from the coal-substance in each case. The residues were dried in an atmosphere of nitrogen and their coking powers compared with those of the original coals. Each yielded just as strong a coke as did the original coal. It may therefore be concluded quite definitely that the coking properties of these coals do not depend upon the presence in them of free resins.

With regard to the characters of the extracts obtained in the last-named experiments, it may be remarked that: (a) those removed by ether were brownish-yellow substances of the consistence of vaseline and strongly fluorescent in solution; (b) the alcohol-extracts were dark brown brittle masses suggesting resins in appearance; whilst (c) the benzene-extracts were soft dark brown solids resembling natural bitumens, and strongly fluorescent in solution. The amounts of such extracts obtained in the experiments were insufficient to allow of more than a general examination of them being made.

It is, of course, well known that the extraction of coal with certain basic solvents, such as pyridine, completely destroys the coking power. Such result, however, is not due to the mere removal of resins, but rather to the depolymerising action of the pyridine upon the coal-substance.\* We were therefore led to try the effect of extracting the two hard coking coals, A (Durham) and C (Spanish), with symmetrical tetrachlorethane ( $\text{CHCl}_2\text{—CHCl}_2$ ), in an atmosphere of nitrogen at ordinary pressure. This liquid is not only a powerful solvent for resins, but it also, as we found, attacks and decomposes the coal-substance. On making the experiments, it was found that the coking powers of the two coals in question were utterly destroyed by only one day's Soxhlet extraction with this solvent. Hydrogen chloride was evolved during the process, and some water was formed by decomposition of the coal-substance. The residues contained chlorine, and they actually weighed more than the coal originally taken.

Some similar extraction experiments were made with trichlorethylene ( $\text{CHCl}:\text{CCl}_2$ , b.p.  $85^\circ$ ), and also with chloroform (b.p.  $61^\circ$ ), as solvents. In the case of trichlorethylene, no hydrogen chloride was evolved during the actual extraction, but it was eliminated when the residues were carbonised. The residues, however, all coked strongly. Chloroform had a still milder action on the coals; the amounts of extractive matter removed by it in three to five days' Soxhlet extraction were as follows:—

\* See Bone and Sarjant, *loc. cit.*, p. 132.



Table VI.—Soxhlet Extraction of Coking Coals by Chloroform.

Coal.	Percentage extract.
A. (Durham) .....	3.27
B. (Barnsley) .....	5.13
D. (Spanish) .....	3.48
F. (Welsh) .....	1.20

No hydrogen chloride was evolved, and the coking powers of the residues were in each case unimpaired. It should here be mentioned, however, that, at one stage of our inquiry, experiments were tried upon the effect of passing a stream of chloroform vapour over the Durham and Spanish coals A and D, maintained at temperatures between 220° and 270° C. It was found that hydrogen chloride appeared at 220°, and that its evolution increased rapidly as the temperature was raised beyond that point. It was evident that the coal-substance was being attacked chemically, with the result that the coking power of the Durham coal had deteriorated somewhat, whilst that of the Spanish coal was entirely destroyed. Control experiments, in which the coals were similarly heated in a current of nitrogen, showed no deterioration of the coking power.

We conclude from this series of experiments:

(1) That the coking propensities of coals are not mainly due to the presence in them of free resins; but

(2) That they may be destroyed by the action of any solvent or vapour which will either depolymerise the coal-substance (as pyridine does) or radically alter it by chemical interaction (as is the case with tetrachlorethane).

#### C. *A Method of Isolating Coal-Resin.*

During the investigation it had become evident that rather a large quantity of a coal must be extracted in order to obtain from it enough of the resinic constituents for a thorough examination of them. The usual Soxhlet method was manifestly unsuitable for such purpose; also an extraction of the coal by pyridine alone was objectionable, on account of the depolymerising action of this solvent upon the non-resinous matter. We had, therefore, to devise some other process for the isolation of resins from coal which would minimise this disadvantage. After numerous trials, we were finally led to employ a mixture of equal parts of pyridine and amyl alcohol as a more suitable medium, and to substitute for the Soxhlet apparatus a two-gallon metal canister fitted with a reflux condenser, and also with a tube reaching nearly to the bottom through which a current

of inert gas (*e.g.*, nitrogen) could be passed so as to avert oxidation during the extraction process.

The experimental procedure was substantially as follows:—

One kilogramme of the dried coal, ground to pass a 60-mesh sieve, was added to 3 litres of a mixture of equal volumes of pyridine and amyl alcohol contained in the canister. The contents were boiled for periods varying from 10 to 60 hours, a slow stream of nitrogen being maintained through the apparatus meanwhile. According to our experience, the employment of such a mixture as the extracting medium greatly mitigates the “unbuilding” action of undiluted pyridine upon the coal-substance\* without materially impairing its solvent action upon the resinic constituents thereof. At the end of the said extraction period the solution was separated from the residue, either by filtration on a Buchner funnel at the pump, or by sucking off the solution through an alundum cylinder immersed in it. The latter method was the more expedient, because it minimised exposure to the air. The resulting clear solution was then concentrated to about one-fifth of its bulk by distillation. The remainder of the mixed solvent was removed by distillation, under 20 mm. pressure, in a special form of steam-jacketed vacuum still.

The crude extract thus obtained was a brownish black magma. It varied in amount according to the time of extraction allowed; but subsequent investigation showed that the amount of resin finally obtained from it did not vary materially with the time taken, indicating that such resin had been mostly extracted during the first 10 or 20 hours.

The first step in the purification of the crude extract consisted in dissolving out its resinic part by boiling it with ethyl ether in a reflux apparatus. The ethereal solution was washed with dilute sulphuric acid, to remove last traces of pyridine, and then with water. It was next distilled down to small bulk, and the concentrated solution transferred to an apparatus where it was steam-distilled for 6 hours or more, in order to remove all traces of amyl alcohol. Whilst still hot, the contents of the apparatus were poured into a basin, in which they were allowed to cool, when a brittle button of resinous appearance was obtained. This was roughly dried between filter paper and afterwards powdered and completely dried *in vacuo* over sulphuric acid. It will be referred to hereafter as Resin-extract A.

The portion of the pyridine-amyl alcohol extract which was insoluble in ether was non-resinous; it could be further resolved by normal alcoholic potash solution into (i) an alkali-soluble part; and (ii) an alkali-insoluble part. For the further examination of these products, see below.

*Purification of the Resin-extract A.*—The yield of Resin-extract A from

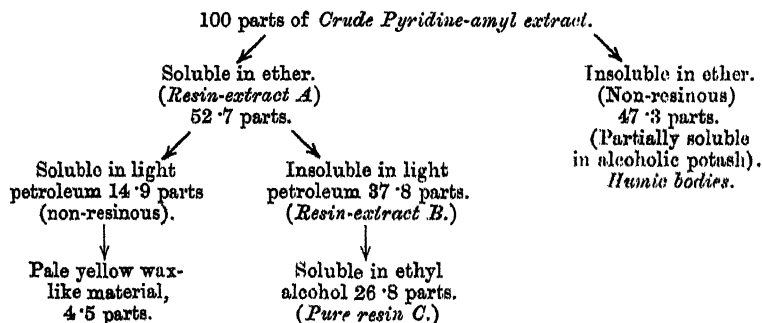
\* *Vide* Bone and Sarjant, *loc. cit.*, p. 132.

the Durham and Barnsley coals (the only ones tried) varied from 1·27 to 2·75 per cent. of the weight taken. The extract softened at about 60° C., and on analysis it proved to be free from sulphur and nitrogen. The ultimate composition of one specimen derived from the Barnsley coal was found to be :—

	Per cent.
Carbon .....	80·13
Hydrogen .....	7·13
Oxygen (by difference) .....	12·74
	<hr/>
	100·00

Further investigation proved the material to be a mixture, and it was therefore separated into two portions by extraction with light petroleum (b.p. 40°–60°) in a Soxhlet apparatus. This solvent removed a non-resinous waxy constituent, which, on subsequent refining by means of sulphuric acid, was finally obtained as a pale yellow substance, resembling soft paraffin in appearance. The residue, insoluble in light petroleum, was resinous in character (Resin-extract B); it was further purified by solution in cold ethyl alcohol, yielding a pure resin (Resin C).

The following scheme shows the results of subjecting the Barnsley coal B to the treatment outlined above :—



There have thus been isolated from the coal :—

- (1) A non-resinous wax-like substance, soluble in light petroleum.
  - (2) A resin, insoluble in light petroleum, but soluble in alcohol.
  - (3) Non-resinous substances of "humic" type, insoluble in light petroleum.
- These will now be further described as follows :—

(1) *The non-resinous wax-like substance* amounted in all to about 0·35 per cent. of the original coal. On purification with sulphuric acid it yielded a pale yellow substance with the appearance of a soft paraffin, which did not

absorb bromine. This substance was free from nitrogen and sulphur, and on analysis was found to contain :—

	Per cent.
Carbon .....	86.00
Hydrogen .....	10.80
Oxygen (by difference) .....	3.20
	<hr/>
	100.00

The substance was soluble in ether, chloroform and most other organic solvents, its solutions having a characteristic green fluorescence. The amount isolated was too small to permit of further investigation.

(2) *The Resin*.—This was a translucent solid of deep red colour in mass, but amber-yellow when powdered. It had a conchoidal fracture and was completely soluble in ethyl ether, alcohol, acetone, benzene, acetic acid and chloroform; but it was insoluble in light petroleum. It began to soften at a temperature just above 100° C. The resin was free from nitrogen and sulphur, its ultimate composition being as given below. It resembled a “resene” in its chemical inertness. Two determinations of its molecular weight by the ebullioscopic method (Beckmann apparatus), using ethyl alcohol as solvent, gave (i) 453.0 and (ii) 450.7. These values, and the ultimate composition agree well with the empirical formula  $C_{31}H_{32}O_3$  (Mol. Wt. 452.0):—

	Found.	Calculated for $C_{31}H_{32}O_3$ .
Carbon .....	82.15	82.30 per cent.
Hydrogen .....	7.11	7.08 „
Oxygen (by difference) .....	10.74	10.62 „
	<hr/>	<hr/>
	100.00	100.00

The total amount of the purified resin finally isolated from the two coking coals used did not much exceed 1 per cent. of their weight; and we think this figure (or perhaps something between it and 2 per cent.) may be accepted as an approximately correct indication of the proportion of true resin in such coals.

(3) *The Humic Substances*.—These constituted the portion of the crude pyridine-amyl alcohol extract which was insoluble in ether. They may also be obtained (as we found later) by extracting coal with pyridine alone, and then treating the pyridine extract, first with ether to remove the resinous and waxy substances, and then with chloroform, which dissolves these humic bodies. It may be remarked that the term “humic” is here used as a

convenient designation for these compounds, because it is a generic term, denoting the brown or black products resulting from the condensation or dehydration of celluloses and carbohydrates generally under the influence of acids or bacterial agencies. And there is strong reason for believing, as will appear later, that the substances which we are now discussing are chiefly of cellulosic origin although they also contained some nitrogenous material. From the method of their isolation, it would appear that these humic bodies constituted a considerable part of the "resinic constituents" which Clark and Wheeler obtained by the pyridine-chloroform extraction method referred to in the introduction to this paper.

The Durham coal yielded about 4 per cent. of its weight of these humic bodies. They formed a deep brown mass, chocolate-coloured when finely powdered, and were partially soluble in an alcoholic solution of potash. The resulting solution was colloidal, and on saturating it with either hydrogen chloride or carbon dioxide, a brown flocculent precipitate was thrown down, which when dried had the composition :—

	Per cent.
Carbon .....	76.25
Hydrogen .....	5.15
Oxygen (by difference)* .....	16.85
Nitrogen .....	1.75
	<hr/> 100.00

A noteworthy point about this acidic substance was that, when the flocculent precipitate was freshly filtered off, it formed a bulky dark-coloured opaque jelly; but when the latter was subsequently dried it shrank enormously, finally leaving a brittle lustrous black structureless mass, with conchoidal fracture, resembling the Oolitic coal, H, or those bright bands in bituminous coals which Stopeš† has named "vitrain." This characteristic behaviour suggests that such "vitrain" may have been formed from a colloidal gel, and we propose in future experiments to explore further this aspect of the matter.

Both the humic bodies as a whole, and also the acidic part of them described above, when slowly heated in an apparatus similar to that used by Hollings and Cobb,‡ showed a strongly exothermic decomposition within the temperature range 275° to 375° C. Cellulose itself showed a similar evolution of heat at about 350°, as indeed Hollings and Cobb had previously

\* The oxygen figure would include a little sulphur, which was not separately determined, owing to the small amount of material at our disposal.

† 'Roy. Soc. Proc.,' B, vol. 90, p. 470 (1919).

‡ 'Journ. Chem. Soc. (Trans.),' 1915, p. 1106.

proved. These facts strongly suggest that the "humic" constituents here in question are chiefly of cellulosic origin; but the further development of this important aspect of the question is reserved for a future communication.

*D. Experiments on the Coking Principle of Coals.*

The constituents of coal described above having been thus separated, and to some extent characterised, it remained to test their relative influences in the formation of coke. This was done in the following manner:—

Each of the substances was mixed in varying proportions with a dry coke which had previously been prepared at 900° C., and ground to pass a sieve of 30 meshes to the inch. Intimate mixture was assured either by grinding the materials together in an agate mortar or by dissolving the coal-constituent under examination in a suitable solvent, absorbing the solution on a weighed quantity of the coke-dust and drying off the solvent at a gentle heat. Ten grammes of every such mixture were then placed in a cylindrical iron vessel of about 1 inch internal diameter. The bottom of this vessel was closed by an iron plate firmly held in position by screws, and into the top was passed a solid iron cylinder, weighing about 100 grm., and making a good sliding fit into the coking chamber, so as to hold the charge together, while allowing any gaseous products to escape, during the subsequent heating operation.

The vessel thus charged was placed at once into an electric muffle furnace at 850–900°, and left there for 6 or 8 minutes, by which time all smoke and flame were spent. It was then taken out and allowed to cool. Using 9 grm. of coke-dust and 1 grm. of each ingredient (*i.e.*, 10 per cent. mixtures), the following results were obtained:—

- (1) The non-resinous waxy material, soluble in petroleum ether, gave a pulverulent residue.
- (2) The resin gave a coke-like product firm enough to be tested as to its crushing strength.
- (3) The alkali-soluble humic material gave a similar coke-like product about equal in strength to that obtained with the resin.
- (4) The chloroform-soluble humic material gave a good firm "coke."
- (5) The portion of the pyridine extract which was insoluble in chloroform gave, in 10 per cent. mixture, a pulverulent residue. Alone, or in 50 per cent. mixture with coke-dust, it gave a weakly coherent residue.

The crushing strengths of various "cokes" prepared in the above manner were now measured in a cement-testing machine. For this purpose the end faces of the specimens were ground down so as to give cylindrical blocks exactly 18 mm. high, on which the tests were performed. The following

figures show the relative crushing strengths, in lbs. per square inch, of specimens prepared from the intimate mixtures of coke-dust with (*a*) the untreated Durham coal; (*b*) the "humic" material obtained from the Durham coal; and (*c*) a similarly prepared humic extract from the slightly coking Nigerian coal mentioned in the introduction to this paper.

Table VII.—Crushing Strengths of the "Cokes."

Percentage of binding ingredient used.	Binding material employed.		
	Durham coking coal.	Humic matter extracted from	
		Durham coal.	Nigerian coal.
5	—	100	
10	Pulverulent }	1. 100	1. 60
		2. 150	2. 125
20	125 }	1. 400	1. 225
		2. 420	2. 300
30	260		
40	1. 325 }		
	2. 550 }		
	1. 190 }		
50	2. 175 }		

No test could be obtained with the mixtures containing 30 per cent. of the humic material, because they intumesced to such an extent as to be forced out of the coking vessel. Both the pure coal-resin, and the alkali-soluble portion of the humic material,\* had a considerable cementing power, 10 per cent. mixtures of them giving crushing tests of 130 and 125 respectively. But, inasmuch as the resin only constitutes about 1 per cent. of the coals which we have so far tested, it can hardly play a great part in the formation of coke from them.

It will be seen from the figures above quoted that, what we have termed the "humic" extracts (even that prepared from the Nigerian coal) have a strong cementing effect; but whereas the weakly-coking Nigerian coal yielded only 1·7 per cent. of these bodies, the strongly coking Durham coal yielded 4 per cent. of them.

We do not wish to imply that the coking propensities of the two coals depended simply and solely upon these figures; because it may be that such "humic" extracts as were used in the experiments did not exist in the free state in the original coal, but were liberated by the action of pyridine upon it.

\* Obtained by acidifying its alcoholic potash solution, and subsequently collecting the resulting reddish-brown flocculent precipitate by filtration at the pump, washing it with cold dilute alcohol, and finally drying it *in vacuo* over sulphuric acid.

Nevertheless, though present in the coal possibly in a state of loose combination (or polymerisation), they may well be liberated, during the chemical upheaval that takes place during carbonisation, and by their subsequent decomposition play a determining part in the cementation of the residual coke.

It is therefore probable, as Clark and Wheeler surmised, that the "binding principle" of coking coals lies chiefly in the chloroform-soluble portion of their pyridine extracts; but, according to our experiments, it is not "resinic" in origin. It appears rather to consist of a series of "humic" transformation products of cellulose, of varying complexity. The simpler members of this series are soluble both in chloroform and in alcoholic alkali; and they are also easily fusible. Indeed some of the most soluble, obtained as a yellow powder by fractional precipitation from hot alcohol, melted below 100° C. Further up the series these substances become insoluble, even colloiddally, in alkali, though they are still soluble in chloroform; also, their temperature of fusion rises so as to approach nearly that of their decomposition. The members up to this point, apparently, are the chief binding agents in coke-formation, and although not necessarily present in the free state in the raw coals, they exist in a state of loose combination therein, from which they are liberated by a moderate degree of heat. Higher still up the series there are more complex bodies of cellulosic origin which are insoluble in chloroform, though still extractable by pyridine. These, and the yet more complex substances insoluble in pyridine, decompose without fusion, and thus have little or no binding power.

#### *Summary and Conclusions.*

The results of the investigation, taken as a whole, lead to the following conclusions:—

- (1) That strongly-coking bituminous coals may be extracted for prolonged periods by organic resin-solvents without impairing their coking propensities.
- (2) That the pyridine-chloroform method of extracting coals does not, as Clark and Wheeler have claimed, effect "a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated"; but that, on the contrary, it yields an admixture of resins with a predominance of non-resinous substances, which latter are chiefly of cellulosic origin, and have been provisionally designated "humic" bodies in this paper.
- (3) That resins may be extracted and isolated in a pure condition from such coals by means of pyridine-amyl alcohol treatment, following by successive treatments with ethyl ether and light petroleum, in the manner described in Section C hereof, but that these resins probably do not normally much



exceed 1 per cent. of the coal-substance, and, although they may be a contributory, are not usually the chief cause of the coking propensities of coals.

(4) That there can also be obtained from such coals, by the special pyridine or pyridine-amyl-alcohol treatments described in Section C hereof, a series of non-resinous substances, which are, for the most part, insoluble in ether but soluble in chloroform, and that the yield of such bodies may amount to as much as 4 per cent (or even more) in the case of strong coking coals.

(5) That the aforesaid non-resinous substances on being heated, out of contact with air, give a strong exothermic reaction between 275° and 375° C. accompanied by the elimination of water, which behaviour resembles that of cellulose, showing them to be chiefly cellulosic in type and origin.

(6) That the coking propensities of coals are principally due to the presence, or the formation in them by heat, of such non-resinous substances of cellulosic origin as aforesaid, whose fusion temperatures are below those at which they undergo rapid decomposition.

(7) That the yet more complex substances, also of cellulosic origin, which form the main portion of the coal-substance, but which decompose without fusion, have little or no direct influence upon its coking propensities.

In conclusion, it should be stated that the participation of one of us (A. R. P.) in the investigation was made possible by a grant from the Department of Scientific and Industrial Research, to which due acknowledgment is hereby gladly made, and that the research is being continued with such aid. We also desire to acknowledge the valued assistance of Mr. A. R. Godfrey, A.R.C.S., in connection with the new method of isolating coal-resin described in Section C of the paper. Finally, we are much indebted to Messrs. Minero Siderurgica de Ponferrada, S.A., of Madrid, and to Mr. H. M. Morgans (formerly their Engineer), for their kind permission to include in this paper the references to the interesting Spanish coals upon which we experimented.

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*The Minimum Electron Energies Associated with the Excitation  
of the Spectra of Helium.*

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(Communicated by Prof. Sir E. Rutherford, F.R.S. Received December 16, 1921.)

[PLATE 13.]

*Introduction.*

In addition to the orthohelium and parhelium serial systems, the spectrum of helium includes the lines of the enhanced system and the many-lined, or band, spectrum. The lines of the orthohelium and parhelium series are attributed to transitions of electrons within uncharged helium atoms, while the enhanced lines are attributed to the transitions of the remaining electrons in already ionised helium atoms. It has been suggested that the band spectrum of helium arises from disturbances of helium molecules ( $\text{He}_2$ ), for the formation of which electrical excitation is postulated as a preliminary condition.\*

On the view that each of the lines of the orthohelium and parhelium series corresponds to a definite transition of one of the electrons in the normal helium atom, it might be expected that it would be possible to excite certain of the series lines without exciting others by suitably adjusting the disturbing force, so as to make the occurrence of certain transitions impossible. The investigations of Rau,† of Horton and Bailey,‡ and of Compton and Lilly,§ have led to the conclusion that it is not possible to excite certain of the orthohelium and parhelium series lines without exciting all of them. This conclusion is in complete agreement with the work of McLennan and Ireton,|| and of Foote and Meggers,¶ on the spectra of metallic vapours. These investigators found that the only lines which could be excited without all the lines appearing were the first lines of the series whose limiting frequencies corresponded to the respective ionisation potential differences of the metallic vapours concerned, a result which was supported

\* W. Lenz, 'Deutsch. Phys. Ges. Verh.,' vol. 21, p. 632 (1919), and A. Sommerfeld, 'Atombau und Spektrallinien,' p. 563.

† H. Rau, 'Würzburg Phys. Med. Ges. Ber.,' February, 1914.

‡ F. Horton and D. Bailey, 'Brit. Ass. Reports,' 1919, p. 153.

§ K. T. Compton and E. G. Lilly, 'Astro.-Phys. Journal,' vol. 52, p. 1 (1920).

|| J. C. McLennan and H. J. C. Ireton, 'Phil. Mag.,' vol. 36, p. 450 (1918).

¶ P. D. Foote and W. F. Meggers, 'Phil. Mag.,' vol. 40, p. 80 (1920).

by the current-potential difference curves of Tate and Foote,\* and of Mohler, Foote and Meggers,† etc. These observers found that the only types of inelastic impacts, which occurred between atoms of the metallic vapours and electrons, were those corresponding to the ionisation of the atom, and to the voltages which were connected by the quantum relation with the frequencies of the first lines of the series whose limits were connected with the ionisation potential differences. The lines of the helium spectrum which, by analogy with the cases of the metallic vapours, might be expected to appear before the other helium lines, are in the extreme ultra-violet region of the spectrum, and could only be detected with a vacuum grating spectroscopet: this was not used by either of the investigators to whose work in helium reference has been made.

A different result was obtained by Richardson and Bazzoni,§ who came to the conclusion that a genuine difference of about 0.5 volt existed in the energies required for the excitation of  $\lambda 4472$  and  $\lambda 5876$ , and a difference of 0.25 volt between the energies required for  $\lambda 4713$  and  $\lambda 5876$ , the latter line appearing at the lower voltage in each case.

In a recent research by Franck and Knipping|| on the potentials of excitation of helium, these experimenters have obtained a series of bends in their current-potential difference curves at voltages intermediate to the minimum voltage for inelastic impact and the minimum ionisation voltage. These bends are interpreted as indicating the excitation of different ultra-violet series lines, one by one, as the corresponding electron energy is acquired. This would mean that at each bend in the curve a new set of interorbital transitions became included in the transitions possible for the given value of the exciting electron energy, and it therefore suggests that different amounts of energy are required for the excitation of different lines in the orthohelium and parhelium series. Franck and Knipping's interpretation

\* J. Tate and P. D. Foote, 'Phil. Mag.,' vol. 36, p. 64 (1918).

† F. L. Mohler, P. D. Foote, and W. F. Meggers, 'Bur. Stan.,' 1920, p. 734.

‡ It has been shown (Horton and Davies, 'Phil. Mag.,' vol. 42, p. 746, 1921), that the radiations which are emitted at the two critical radiation voltages found in helium can be absorbed and re-emitted by other helium atoms. This effect would result in a "scattering" of these radiations in a vacuum grating spectroscope, and might prevent them from being detected, thus accounting for the fact that, in his earlier researches on the extreme ultra-violet spectrum of helium, Lyman obtained no trace of lines corresponding to these critical voltages. It therefore seems probable that the line at  $\lambda 585$  (the wave-length corresponding to the higher critical radiation voltage in helium), recently detected by Fricke and Lyman ('Phil. Mag.,' vol. 41, p. 814, 1921) does not originate from the helium itself. The fact that no line was detected at the wave-length corresponding to the lower critical radiation voltage supports this suggestion.

§ O. W. Richardson and C. B. Bazzoni, 'Nature,' vol. 98, p. 5 (1917).

|| J. Franck and P. Knipping, 'Zeits. f. Phys.,' vol. 1, p. 320 (1920).

of the bends in their curves involves the acceptance of certain views with regard to the particular electron transitions which give rise to the orthohelium and the parhelium series lines, and, on the basis of these views, the order of appearance of the different lines for increasing values of the voltage, and the particular values of the potential differences at which certain lines should be excited, can be calculated.

The views referred to are that the orthohelium and parhelium principal series are concerned with transitions involving a return of the displaced electron within a helium atom to the orbits to which electrons are removed at the first and second, respectively, of the critical voltages at which photo-electrically active radiations have been detected in the current-voltage curves. Investigations of the production of radiation and of ionisation in helium have shown that the minimum radiation potential difference is 20·4 volts and that the minimum ionisation potential difference is 25·2 volts. The difference between these two critical voltages is 4·8 volts, a value which is in good agreement with the voltage 4·78 connected by the quantum relation with the limiting frequency of the orthohelium principal series. It therefore seems reasonable to associate this series with the orbit to which an electron within a helium atom is removed as the result of an inelastic impact with an electron having 20·4 volts energy. The second critical radiation voltage, 21·2 volts, was not detected until its existence had been foreshadowed from theoretical considerations by Landé,\* who attributed the existence of two independent serial systems in the helium spectrum to the existence of two independent sets of outer orbits. According to Landé, one of these sets of outer orbits, namely, the set of orbits associated with the orthohelium series, is coplanar with the orbit of the undisturbed electron, while the plane of the set of orbits associated with the parhelium serial system is at angle with the plane of this orbit. The limiting frequencies of the orthohelium and parhelium principal series are connected by the quantum relation with the voltages 4·78 and 3·98 respectively, so that the energy required to remove an electron in a normal helium atom to the orbit from which the parhelium principal series originates must be  $(4·78 - 3·98 =) 0·8$  volt higher than 20·4 volts. The existence of a second radiation voltage at 21·2 volts has been found experimentally by Franck and Knipping,† and by Horton and Davies.‡ In their more recent paper, Franck and Knipping describe experiments from which they conclude that though inelastic collisions occur when electrons with 20·4 volts energy collide with helium atoms, such collisions are not followed

\* A. Landé, 'Phys. Zeits.,' vol. 20, p. 228 (1919).

† J. Franck and P. Knipping, 'Phys. Zeits.,' vol. 20, p. 481 (1919).

‡ F. Horton and A. C. Davies, 'Phil. Mag.,' vol. 42, p. 746 (1921).

by an emission of radiation unless there is impurity present in the helium. These conclusions confirm Franck and Reiche's suggestion\* that the abnormal coplanar helium atoms, which result from 20·4-volts impacts, are "metastable," a suggestion which follows from their hypothesis that the normal state of the helium atom is identical with the unit quantum sharp series state of the crossed system of orbits. This hypothesis has been criticised on theoretical grounds by Kemble,† while the conclusions drawn by Franck and Knipping have been criticised by Horton and Davies.

Franck and Knipping have identified the bends in their curves in helium, intermediate to the radiation voltage 21·2 and the ionisation voltage, with the excitation of successive lines of an ultra-violet series whose first term corresponds to 21·2 volts, and whose last term corresponds to the ionisation voltage, because by adding to 21·2 volts the potential differences corresponding to the successive terms of the parhelium principal series, *i.e.*, the series originating from the 21·2-volts orbit, they obtained good agreement between the calculated values of the potential differences corresponding to the excitation of successive lines of this ultra-violet series, and the potential differences at which the bends occurred. The absence of bends at the voltages obtained by adding to 20·4 volts the potential differences corresponding to the successive frequencies of the orthohelium principal series lines, is interpreted by Franck and Knipping as being due to the fact that, except in special circumstances, transitions between the crossed and coplanar systems cannot occur. When displacements to the coplanar system of orbits have occurred, the electrons are supposed to return to the 20·4-volts orbit (not to the normal orbit), so that the resulting lines of the orthohelium system would be of too long a wave-length to produce photoelectrons and so to give an indication in the curves.

The minimum voltages at which certain lines of the orthohelium and parhelium series might be expected to appear, if direct transitions from the normal orbit to the orbit from which the electron has to fall to give rise to the particular line in question were possible in each case, have been calculated on the view that these systems are associated with the 20·4 volts orbit and the 21·2 volts orbit respectively. These values are given in Table I. The letters S, P, D, are used in designating terms of the sharp, principal, and diffuse series of parhelium, and the letters *s*, *p*, *d*, for the corresponding series of orthohelium. Table II gives the voltages which have been calculated in the case of some of the lines, on the assumption that direct displacements from the normal orbit, other than those occurring at 20·4 volts and 21·2 volts, can

\* J. Franck and O. Reiche, 'Zeits. f. Phys.,' vol. 1, p. 54 (1920).

† E. C. Kemble, 'Phil. Mag.,' vol. 42, p. 123 (1921).

only take place to principal series orbits, as is suggested by the positions of the discontinuities in Franck and Knipping's curves, but that there is no limitation of the possible transitions as the displaced electron returns to the normal orbit. According to Table I, a difference of 0·7 volt should exist between the voltages at which  $\lambda$  5876 and  $\lambda$  4472 appear. This is a little higher than the difference recorded by Richardson and Bazzoni. According to the same Table the difference between the voltages at which  $\lambda$  5876 and  $\lambda$  4713 should appear is 0·6 volt, which is more than double the difference recorded for these two lines by the above experimenters. Table II, on the other hand, which is based on an assumption for which there appears to be more justification, gives differences which are smaller than those recorded by these observers. The two pieces of evidence in favour of the view that the different lines of the orthohelium and parhelium series can be excited at different voltages are thus not in agreement with one another.

Table I.

Wave-length.	Series.	Exciting voltage.	Wave-length.	Series.	Exciting voltage.
7066	2, $p-m, s$	23·3	4922	2, $P-m, D$	24·3
7282	2, $P-m, S$	23·5	3965	2, $S-m, P$	24·3
3889	2, $s-m, p$	23·6	4438	2, $P-m, S$	24·6
5876	2, $p-m, d$	23·6	4026	2, $p-m, d$	24·6
6678	2, $P-m, D$	23·7	4388	2, $P-m, D$	24·6
5016	2, $S-m, P$	23·7	4121	2, $p-m, s$	24·6
4713	2, $p-m, s$	24·2	4169	2, $P-m, S$	24·8
5048	2, $P-m, S$	24·3	4144	2, $P-m, D$	24·8
3188	2, $s-m, p$	24·3	4024	2, $P-m, S$	24·9
4472	2, $p-m, d$	24·3			

Table II.

Wave-length.	Series.	Exciting voltage.	Wave-length.	Series.	Exciting voltage.
3889	2, $s-m, p$	23·6	3188	2, $s-m, p$	24·3
7066	2, $p-m, s$		5876	2, $p-m, d$	
			4713	2, $p-m, s$	
			3965	2, $S-m, P$	24·3
5016	2, $S-m, P$	23·7	4922	2, $P-m, D$	
6678	2, $P-m, D$		5048	2, $P-m, S$	
7282	2, $P-m, S$		4472	2, $p-m, d$	24·6

In addition to the critical voltages already mentioned, it has been shown, both by Franck and Knipping,\* and by Horton and Davies,† that there is

\* 'Phys. Zeits.,' vol. 20, p. 481 (1919).

† F. Horton and A. C. Davies, 'Phil. Mag.,' vol. 39, p. 592 (1920).

another critical value at about 80 volts, at which point further ionisation of helium takes place. The increased production of ionisation is attributed to the removal simultaneously of both electrons from the helium atom. Horton and Davies have further shown that when an intense bombarding electron stream is employed, there is an increased production of ionisation at 55 volts, due to the removal of the second electron from helium atoms which have already been ionised by previous collisions. This value is in fair agreement with the value 54.2 volts calculated from Bohr's theory as the energy required to ionise a positively charged helium atom. It would therefore be expected that under suitable conditions the enhanced lines of helium would make their appearance at these critical voltages. The frequencies of these lines are given by Bohr's equation  $\nu = 4N(1/n^2 - 1/m^2)$ . The most easily observed of them is  $\lambda 4686$ , the first line of the Fowler series, given by  $\nu = 4N(1/3^2 - 1/m^2)$ , where  $m$  may have any value from 4 to infinity. Rau (*loc. cit.*) obtained evidence that the line  $\lambda 4686$  was produced at 80 volts but not at 75 volts. In a paper published while the present investigation was in progress, Compton, Lilly, and Olmstead,\* record the observation of this line as low as 55 volts, but never below this value, and they found that its intensity was much increased above 80 volts.

As the frequency of the line  $\lambda 4686$  is given by the equation

$$\nu = 4N(1/3^2 - 1/4^2),$$

the atom will be in a condition to emit the line when the second electron in an ionised helium atom is displaced to orbit 4. Thus an electron would have to acquire the energy corresponding to a potential difference  $V$ , given by  $V = h/e \cdot 4N(1/1^2 - 1/4^2)$ , or 50.8 volts, in order to be able to excite  $\lambda 4686$  on collision with a positively charged helium atom.

It has been mentioned earlier that the view has been expressed by Lenz and by Sommerfeld that the band spectrum of helium arises from disturbances of helium molecules formed by the combination of pairs of electrically excited helium atoms. Franck and Knipping have suggested that the particular type of abnormal helium atom concerned is the abnormal coplanar atom resulting from the 20.4 volts electronic-atomic impacts. These abnormal atoms are held by Franck and Knipping to be "metastable," *i.e.*, they cannot revert to the normal state without first undergoing ionisation, or under the influence of strong electric fields, such as would be generated by the formation of short-lived chemical combinations between the metastable helium atoms and atoms of any impurity present in the gas. In the absence of impurities, these abnormal atoms may either remain in the abnormal state or form  $\text{He}_2$

\* K. T. Compton, E. G. Lilly, and P. S. Olmstead, 'Phys. Rev.,' vol. 16, p. 282 (1920).

molecules. According to Franck and Knipping, the forces generated at the formation of  $\text{He}_2$  molecules are not sufficiently strong to enable the displaced electrons to return to their normal orbits. Horton and Davies have recently shown\* that the radiation which is produced as the result of 21.2-volts electron collisions ionises some systems which result from the 20.4-volts collisions. These systems are presumably abnormal atoms or helium molecules.

The following experiments were therefore made to determine the minimum voltages at which lines of the ordinary serial systems, lines of the enhanced system, and lines of the band spectrum, of helium could be obtained under different conditions of gas pressure and electron current density, with a view to testing whether the association of the band spectrum with the  $\text{He}_2$  molecule can be reconciled with the recent suggestions as to the production of this molecule, and also with a view to testing the possibility of the excitation of lines in the helium spectrum, other than the single line, without ionisation occurring.

*Description of Apparatus, etc.*

Two forms of apparatus were used to investigate the excitation of the helium spectrum, one of which was designed with a view to detecting differences in the voltages required for the stimulation of different lines, and the other with a view to obtaining low voltage arcs. One of these forms of apparatus is shown in fig. 1, which is a section at right angles to the lengths of the filaments. In its main features this apparatus resembled that used by Horton and Davies for the investigation of the production of luminosity in atmospheric neon, and described in detail in their paper.† The present apparatus was fitted with two parallel lime-coated platinum filaments (only one of which was used at a time), in order to avoid delay when a filament burned through. The filaments, F, F, the gauze cylinder, G, and the anode, A, were enclosed, as shown in fig. 1, in a small glass vessel which could be arranged between the pole pieces, N and S,

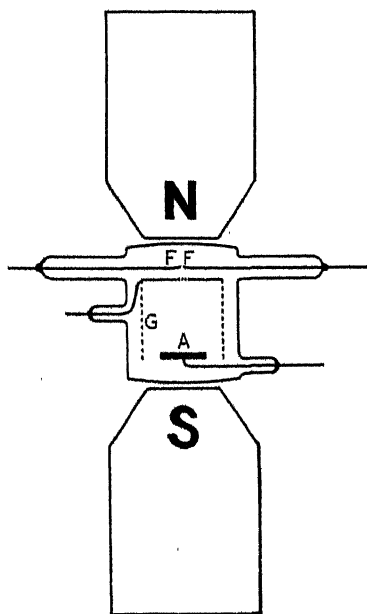


FIG. 1.

\* 'Phil. Mag.,' vol. 24, p. 746 (1921).

† F. Horton and A. C. Davies, 'Phil. Mag.,' vol. 41, p. 921 (1921).



of an electromagnet, which served to concentrate the luminosity into a bright column. By maintaining G and A at the same potential, and controlling the energy of the bombarding electrons by means of a potential difference applied between F and G, it was arranged that these electrons suffered no change of velocity throughout the space viewed by the spectroscope, except that resulting from collisions with helium atoms. The apparatus was arranged so that the lengths of the filaments were at right angles to the plane of the slit of the spectroscope. In this way the maximum concentration of luminosity was obtained in line with the axis of the collimator.

A modification of this form of apparatus was tried, in which both ends of the cylindrical gauze electrode were closed by platinum discs with gauze-covered central holes, and in which the anode, A, was replaced by a second lime-coated platinum filament, arranged 2 mm. below the bottom disc, parallel to the first filament, and in line with this and with the gauze-covered holes. It was anticipated that the simultaneous supply of electrons from opposite directions might facilitate the occurrence of multiple electron impacts, but in practice it was found to be of no advantage, and the form of apparatus finally adopted was that shown in fig. 1.

In the apparatus designed for the investigation of low voltage arcs a filament of fine tungsten wire was employed to supply the bombarding electrons. The apparatus was fitted with three such filaments, so as to avoid delay when one of them burned through. Fig. 2 shows the arrangement of

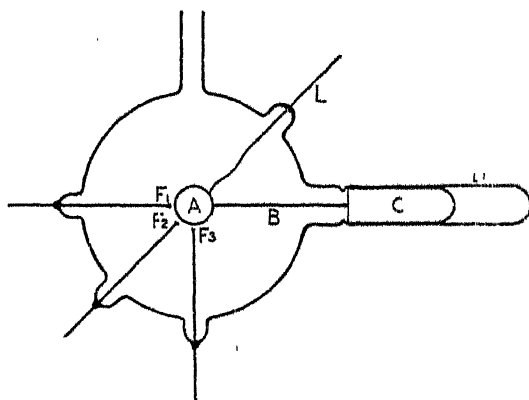


FIG. 2.

the electrodes which was found to be most suitable, the section being in a plane at right angles to the lengths of the filaments, which were parallel to one another. The three filaments,  $F_1$ ,  $F_2$ , and  $F_3$ , were sealed, as shown, into a spherical glass bulb of about 3.5 cm. radius. The anode, A, was a hollow platinum sphere, 1 cm. in diameter, rigidly attached by a stout platinum wire,

B, to the soft-iron piece, C. The wire, L, was connected with the sphere by means of a strip of platinum foil, about 2 mm. wide. The soft-iron piece fitted loosely into the side tube, D, of the enclosing glass bulb, and by means of an electromagnet it could be moved to different parts of this tube, thereby enabling the distance of the anode from the filaments to be varied over a range of about 2 cm. A limit to the forward motion of the anode was provided by a constriction in the tube D, which just prevented it from touching the filament F<sub>1</sub>.

The method used for freeing the helium from hydrogen, and the arrangement employed for admitting the helium to the apparatus, were similar to those described elsewhere.\* Both forms of apparatus were connected independently by side tubes with the carbon purifying tube through which the helium entered, and another tube from the arcing apparatus led through a stopcock and a second U-tube, immersed in liquid air, to the pumps and pressure gauge. The usual precautions were taken for ridding the glass walls and the electrodes of occluded gases.

A Hilger wave-length spectrometer was employed for the examination of the spectrum, and voltages were read on a high resistance voltmeter connected to the negative end of the filament and to the anode. The first appearance of the different lines, as the energy of the electrons was gradually increased, was investigated both visually and photographically. In order to investigate any connection that might exist between discontinuities in the current-potential difference curves and the appearance of a new line, or group of lines, in the spectrum, the current between the electrodes was measured at the same time as the visual observations of the spectrum were made.

The E.M.F. in the circuit was supplied by a 110-volts storage battery, the potential difference across the discharge tube, and the current through it, being regulated by means of series and parallel resistances. The current between the electrodes was read on a Weston milliammeter, provided with shunts, which was placed in series with the discharge tube. In investigating the minimum voltages at which the helium series lines could be stimulated, a potentiometer arrangement, by means of which the potential difference across the discharge tube could be varied in steps of one-tenth of a volt, was employed.

The potential differences measured on the voltmeter were all subject to a correction, to allow for the velocity of emission of electrons from the filament, etc. This correction was estimated in each case from the position

\* 'Phil. Mag.,' vol. 42, p. 746 (1921).

of the ionisation bend in the current-voltage curves, and it has been taken into consideration in the curves given, and in the critical values stated.

During the observations, the carbon tube through which the helium was admitted to the apparatus was immersed in liquid air. In spite of the precautions taken to secure the purity of the helium used in these experiments, the presence of certain spectrum lines, other than those belonging to helium, was detected on some occasions. No lines were, however, detected, visually or photographically, before the helium lines appeared. The most persistent of the impurity lines was the hydrogen line  $H_{\beta}$ , and this was nearly always observed when the band lines were present. It seems probable that the hydrogen originated from the bombardment of the glass walls and metal parts of the apparatus, for, when the apparatus shown in fig. 1 was used, it was found that an intense glow was sometimes obtained, between the back of the filament and the upper glass wall of the apparatus, in the spectrum of which  $H_{\beta}$  could be seen clearly. Moreover,  $H_{\beta}$  could then be seen in the spectrum of the luminosity in any part of the column, even though no sign of its presence was obtained in an equally intense glow before the discharge passed to the walls.

At the highest pressures used, it was sometimes observed that certain of the bright lines in the red and orange, which were present when the helium band spectrum was very intense, appeared to coincide in position with certain of the brightest neon spectrum lines. The results obtained in these exceptional cases were, however, identical with those obtained in the absence of these lines. Under rather special circumstances, the mercury line  $\lambda 5461$  was observed. The particular circumstances are given in detail later in the paper.

*The Excitation Voltages for the Lines of the Orthohelium and Parhelium Series under Different Conditions.*

The values of the minimum voltage at which lines of the orthohelium and parhelium series were first seen as the potential difference was gradually increased, and the stage at which they disappeared as the voltage was backed, varied very considerably in different experiments. There were, however, two limiting values, namely, 25.2 volts, the ionising voltage, and 20.4 volts, the minimum radiation voltage, which were associated with the excitation of these lines under different conditions. For moderate values of the intensity of the electron stream, and a gas pressure of about 1 mm. or less, the lines made their first appearance as, or after, the electron energy reached 25.2 volts, and disappeared, as the voltage was backed, at the same limit. For pressures above about 10 mm., and for intense electron streams,

the lines appeared at 20.4 volts, or at some voltage between 20.4 and 25.2, and disappeared, as the voltage was backed, at 20.4 volts. In some of these cases the lines could be maintained, after having once appeared, at potential differences of about 13 volts. In such cases it was not possible to go on reducing the voltage until the lines vanished at some potential difference still lower, because the voltage eventually reached a value after which all attempts to reduce it still further resulted in an increase of potential difference. There was also a stage intermediate to those already mentioned, and which occurred under conditions of pressure and electron emission intermediate to those given above, when the lines appeared for increasing electron energies, at 25.2 volts, but vanished as the voltage was backed, at some voltage between 25.2 and 20.4.

The pressures which have been given as dividing results of one class from those of another are, however, only approximate, for it frequently happened that the change in the limit for the appearance or disappearance of lines could be effected by means of the heating current alone.

In many instances the lines of the orthohelium and parhelium series made their appearance very suddenly, and all together, as the energy of the bombarding electrons was increased, and there was a simultaneous discontinuity in the current-voltage curve, signifying a marked increase of current. In other instances the lines were seen very faintly at first, and then they gradually grew brighter as the electron energy was further increased. On these occasions, the yellow line,  $\lambda 5876$ , contrary to the predictions of Table II, was generally seen about one-tenth of a volt before the green line,  $\lambda 5016$ , which in turn appeared about one-tenth of a volt before the other lines. In certain instances the lines faded gradually as the voltage was backed, and did not all entirely disappear until 20.4 volts, there being no marked discontinuity in the current-voltage relations accompanying their disappearance. In these cases,  $\lambda 5876$  and  $\lambda 5016$  remained visible for one- or two-tenths of a volt after the other lines had vanished.

It has been shown in the introduction that there seems reason for the view that the orthohelium and parhelium principal series originate from the orbits to which an electron in a helium atom is removed as the result of 20.4 volts and 21.2-volts electron impacts, respectively. On this view, the values given in Table I are the minimum voltages at which the different lines could possibly be excited as the result of single electron impacts. Any limitation of possible electron displacements, such as that which is the basis of Table II, results in higher voltages than the corresponding values in Table I being required for the excitation of the various subordinate series lines of both systems. Since all the voltages given in Table I are greater

than 23 volts, it follows that when lines of the helium spectrum are detected at about 20·4 volts, their presence cannot be due to the displacements of electrons within the atoms by single electron impacts. They must therefore be due to the cumulative effects of two or more electron impacts, and such cumulative effects would produce ionisation. Since the order of disappearance of the lines in this case (when ionisation is known to be occurring) is the converse of the order of their appearance as the potential difference is gradually increased, it is concluded that the detection of  $\lambda 5876$  and  $\lambda 5016$  before the other lines, in a few instances, is due to the fact that these lines are two of the brightest in the visible spectrum of helium at low voltages, and that it does not indicate any difference in the energy required for the excitation of different lines. The results thus indicate that the occurrence of ionisation of the helium atom is essential for the production of any of the orthohelium or parhelium lines.

Whenever members of the orthohelium and parhelium series are observed below 25·2 volts, ionisation of the helium by cumulative effects must thus be occurring. The current-voltage curves in these cases show a marked discontinuity, indicating an abrupt increase of current, either simultaneously with, or shortly after, the first appearance of spectrum lines. This discontinuity is presumably caused by the increase of electron current which results from neutralisation of the space charge of the emitted electrons by the positive ions produced by ionisation of the helium. The increase in the electron current increases the ionisation by cumulative effects very considerably, and hence the spectrum lines can be *maintained* while the voltage is backed below 25·2 volts, in cases when they cannot be *excited* below this value.

When the lines were maintained below 20·4 volts, and the stage below which the voltage could not be further reduced, was passed, the relative intensities of the different series lines at the same potential difference before and after the minimum value were not the same. This is shown by the two last columns of Table III. The first and second columns give the wavelength and the series of the observed orthohelium and parhelium series lines, and the third column gives their intensities (as judged from visual observations) at 19·0 volts, before the minimum value of the voltage was reached. The fourth column of the Table gives the intensities of the same lines at 19·0 volts, after the minimum value was passed. Lines of the orthohelium and parhelium series further in the violet than  $\lambda 4472$  could not be seen in either case and a photographic comparison of this part of the spectrum in the two cases could not be made because, owing to the high temperature at which the filament had to be maintained in order to attain a potential difference of

19.0 volts after passing the minimum value, the discharge could not be left running continuously for the time of exposure necessary to obtain a photograph.

Table III.

Wave-length.	Series.	Intensity before the minimum voltage.	Intensity after the minimum voltage.
7066	2, $p-m, s$	5	1
6678	2, $P-m, D$	15	3
5876	2, $p-m, d$	20	8
5048	2, $P-m, S$	3	3
5016	2, $S-m, P$	15	4
4922	2, $P-m, D$	10	0.5
4713	2, $p-m, s$	10	0.5
4472	2, $p-m, d$	15	3

Since the lowest potential difference at which the orthohelium and parhelium series lines were ever excited (as distinct from maintained) was 20.4 volts, the maintenance of the lines below this value must be due to the presence of atoms which are in an abnormal (more easily ionisable) condition. The number of atoms which are in this condition must remain constant, for no new ions or abnormal atoms can be produced from normal helium by electron bombardment below 20.4 volts, and the fact that the luminous discharge was maintained for long periods at voltages below 20.4, shows that there was no gradual reduction in the number of ionisable atoms present. Therefore, when the lines are maintained at low voltages, the frequency of electron collisions with helium atoms must be such that, on recombination occurring, the returning electron is unable to fall right back to the normal orbit before being again ejected by another impact.\* The current through the discharge tube must in these cases be carried entirely by electrons, for if any of it were carried by helium positive ions the number of these would diminish with time and the glow would not be maintained. The electron current measured in these circumstances is not, however, the value of the electron emission which would normally be obtained for the given values of the heating current and the voltage, because the positive ions present influence the space charge of the emitted electrons. The variation in the extent to which the space charge is influenced with increase of the heating current, and with increase of the series resistance, accounts for the variation in the current-voltage relations with these factors, and also for the reversible character of the changes.

About 13 volts was the minimum value of the potential difference at which

\* It follows on this view that when the spectrum is maintained below 20.4 volts none of the extreme ultra-violet series lines of helium can be present.

lines of the orthohelium and of the parhelium series were maintained in the present research, but there seems to be no reason for regarding this value as a definite minimum potential difference at which it is possible to maintain them.

Examples of current-voltage curves are given in figs. 3 and 4 and in fig. 5. The continuous curve in each case gives the variations of the current as the

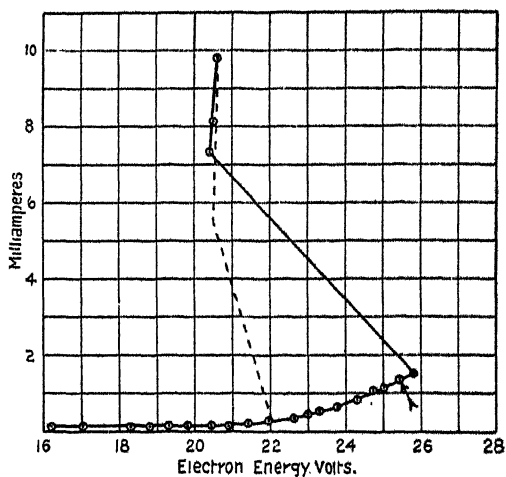


FIG. 3.

The arrow indicates the point at which lines of the orthohelium and parhelium series first appeared.

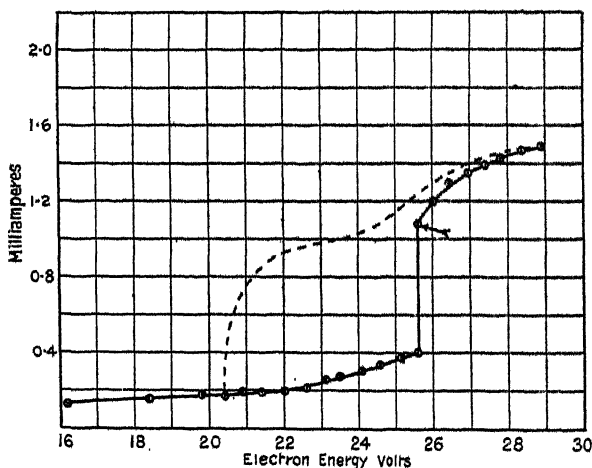


FIG. 4.

The arrow indicates the point at which lines of the orthohelium and parhelium series first appeared.

voltage was gradually increased, and the curve drawn with a broken line gives the corresponding values of the current as the adjustments were made in the

reverse order. The series of observations recorded in figs. 4 and 5 were taken at the same pressure, 19 mm., but the filament temperature was much

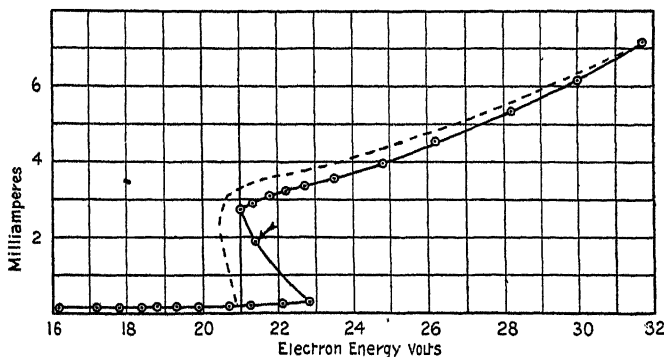


FIG. 5.

The arrow indicates the point at which lines of the orthohelium and parhelium series first appeared.

higher for the series recorded in fig. 5 than for that recorded in fig. 4. The pressure during the observations of fig. 3 was 25 mm. These three curves all show a marked discontinuity at, or near, the voltage at which lines were first detected.

*The Minimum Excitation Voltage for the Line  $\lambda 4686$  of the Enhanced Series, under Different Conditions.*

Under different sets of conditions, three distinct limits were found for the minimum voltage at which  $\lambda 4686$  could be obtained. These limits are the three critical voltages 80.0, 54.2, and 50.8, mentioned in connection with this line in the introduction. About 80 volts was the limit at which  $\lambda 4686$  could be detected visually or photographically when the pressure of helium was 1 or 2 mm. At pressures rather greater than this, 80 volts was the limiting value only when the electron current density was not too high. With intense electron streams at these pressures,  $\lambda 4686$  could be detected down to a voltage of about 54. Whenever  $\lambda 4686$  was seen in the neighbourhood of 54 volts, the lines of the helium band spectrum were always visible, whereas in the circumstances in which 80 volts was obtained as a lower limit, the band spectrum was faint, and in some instances was definitely absent. The photographs 1 and 2 of Plate 13 illustrate this difference in the appearance of the spectrum in the two cases. Both of these were taken using the apparatus of fig. 1. In the case of the first photograph, the voltage across the discharge tube was 96, and the current varied from 2 to 5 milliamperes during the exposure.  $\lambda 4686$  could not be seen below 80 volts under these



conditions. In the case of photograph 2, the voltage varied from 55 to 60 during the exposure of the plate, and the current across the discharge tube varied from 25 to 30 milliamperes. The line  $\lambda 4686$  can be detected in both of these photographs, though in 2 it is not quite so plain as in 1 owing to the presence of the band lines.

The difference in these two photographs corresponds to a definite difference in the current-voltage conditions with respect to a discontinuity in the current-voltage curve, which can best be explained by reference to the curve given in fig. 6. This curve, which is a continuation of a curve corresponding to a series of observations identical with that represented by the continuous curve in fig. 5, shows a discontinuity between 44 and 45 volts. At this discontinuity the helium band spectrum appeared, and there was a marked

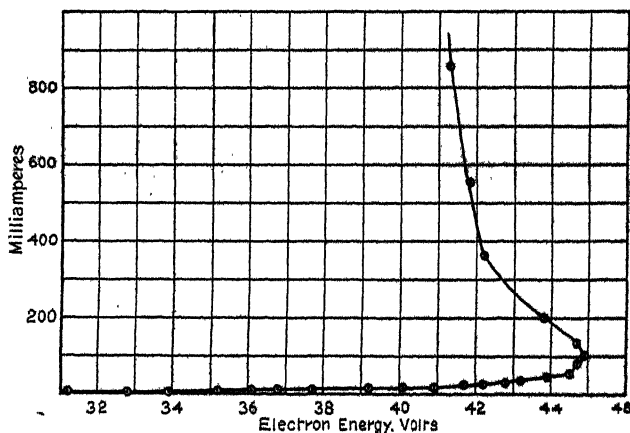
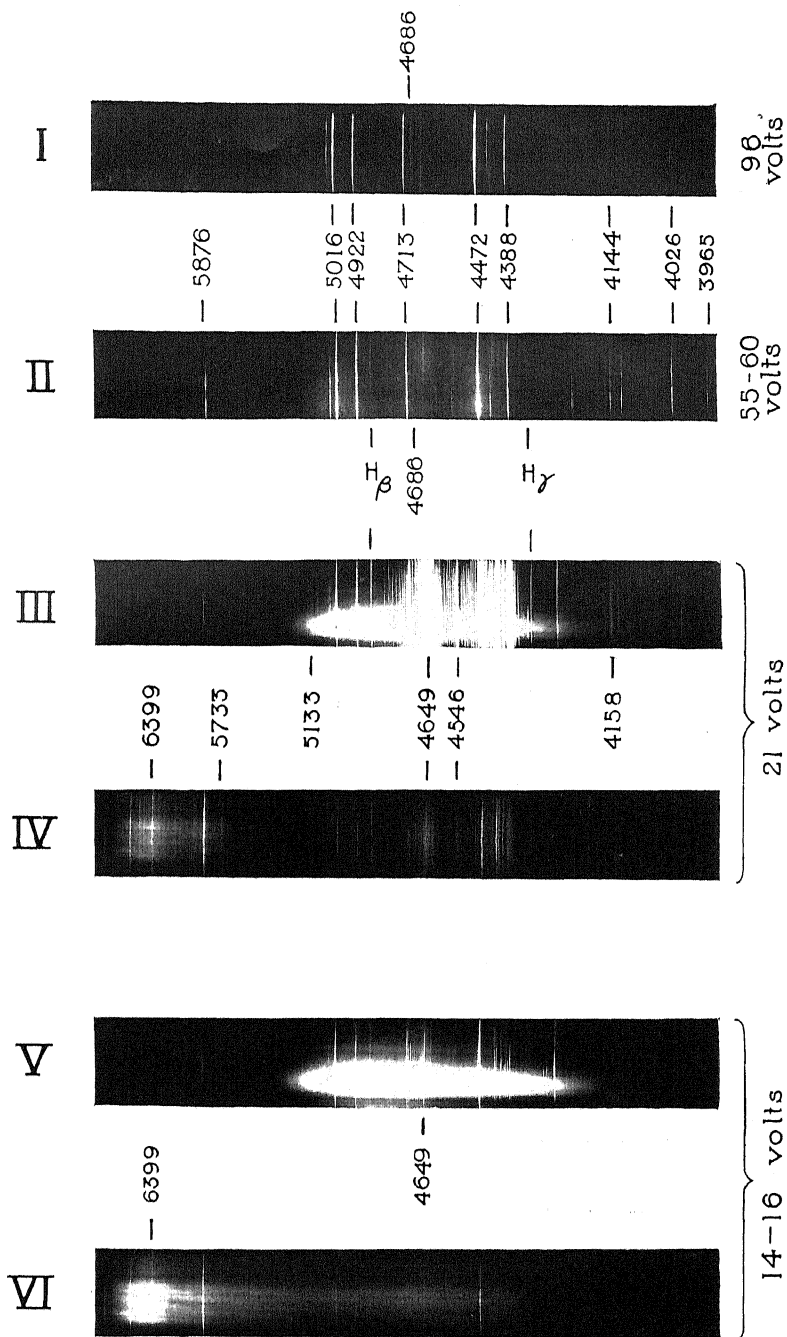


FIG. 6.

change in the appearance of the luminosity, the glow assuming the form of a brilliant arc and becoming more purple in colour. The orthohelium and parhelium series lines made their appearance simultaneously with the occurrence of the discontinuity between 22 and 23 volts, shown in fig. 5. The increase in the current through the discharge tube, and the decrease in the potential difference across it, were sometimes even more marked than in the case given in fig. 6. The voltage at which the second discontinuity occurred did not have any fixed value but depended upon the pressure of helium and upon the intensity of the electron stream, being higher at low pressures and for less intense bombarding streams. At the highest pressures used, *i.e.*, from about 25 to 36 mm., it occurred at the same voltage as the first discontinuity, and the line spectrum and the band spectrum of helium made their appearance together. Photograph 1 was taken when only a small second discontinuity had occurred, while photograph 2 was taken after the occurrence of a marked discontinuity.





In a large number of visual observations under conditions somewhat similar to those in which photograph 2 was taken, the voltage at which  $\lambda 4686$  was first seen to stand out from among the band lines was between 54 volts and 55 volts, indicating a limit at the critical voltage for the further ionisation of the helium positive ion. At still higher pressures and with intense electron streams,  $\lambda 4686$  could first be seen to stand out from the band spectrum lines when the potential difference across the discharge tube was adjusted to about 51 volts. In these cases the band spectrum was more intense relatively to the orthohelium and parhelium series lines than in photograph 2. It was found, however, that for both increasing and decreasing adjustments of the potential difference,  $\lambda 4686$  could be seen to stand out distinctly from the band lines when the voltage was above 50.8. Attempts to see  $\lambda 4686$  below this voltage were unsuccessful.

At pressures from about 20 mm. to 36 mm., the highest pressure used, it was only possible to raise the potential difference across the discharge tube above about 40 volts when the electron current density was too low to cause a second discontinuity in the current voltage relations to occur, and at these pressures the enhanced line  $\lambda 4686$  was not seen at all. This result is in accord with that of Compton, Lilly, and Olmstead (*loc. cit.*) who failed to excite the enhanced lines at any voltage used with pressures above 10 mm.

If 50.8 volts is a genuine limit for the excitation of  $\lambda 4686$ , it may be concluded that the line can be stimulated without further ionisation of the helium positive ion. If, however,  $\lambda 4686$  can be obtained at voltages below 50.8, this conclusion is not justified. It has been shown in the case of the lines of the orthohelium and the parhelium series that these can be excited at voltages intermediate to the ionisation voltage, 25.2, and the minimum radiation voltage, 20.4, this latter value being a limit for their excitation. The corresponding theoretical value in the case of the enhanced lines is 40.6 volts, which corresponds to the energy necessary to produce the fundamental displacement of the remaining electron in an already ionised helium atom, *i.e.*, it is the voltage corresponding to the radiation whose frequency is given by  $\nu = 4N(1/1^2 - 1/2^2)$ . Therefore, if  $\lambda 4686$  could be excited at voltages between 50.8 and 40.6, it would follow that further ionisation of already ionised helium atoms was occurring as the result of cumulative effects. It has already been stated that no evidence of the presence of  $\lambda 4686$  below 50.8 volts was obtained; the results of the present research therefore indicate that the detection of  $\lambda 4686$  between 54 volts and 50.8 volts does not result from the removal of the remaining electron in a positively charged helium atom as the result of cumulative effects, but from single electron impacts on helium positive ions without the occurrence of further ionisation.

*The Minimum Excitation Voltage for the Lines of the Helium Band Spectrum.*

Reference has already been made in the last section to the prominence of the band spectrum of helium after the occurrence of a second marked discontinuity in the current-voltage relations. A more complete account of the conditions under which the band spectrum was seen is given in the present section. The general indications were that it was not present at all until a second discontinuity had taken place. The abrupt increase of current, and the simultaneous fall in the potential difference, which constitute the discontinuity, could be brought about by gradually increasing the temperature of the filament, if the voltage across the tube were sufficiently high.

The value of the voltage after the discontinuity, could be varied to a certain extent by varying the filament temperature, the series and parallel resistances, and the E.M.F. in the circuit, though at each pressure there was a limit below which it could not be reduced. Increase of the E.M.F. in the circuit after this limit had been reached merely increased the current through the discharge without altering the potential difference across it. The limiting value of the final potential difference after the discontinuity depended upon the distance apart of the electrodes and upon the form of the apparatus; for any given form it decreased as the pressure of helium increased. In the case of the apparatus shown in fig. 2, it was found that the lowest limit was obtained when the anode was 2 mm. from the filament. In the present research, about 13 volts was the lowest value obtained, and this occurred when using the apparatus of fig. 2 with helium at about 30 mm. pressure.

Lines of the helium band spectrum could always be seen at the final potential difference after the discontinuity, so that the voltage limit for its detection varied with the pressure of helium in the same way as the limit for this final potential difference varied. The minimum initial voltage at which the changes could be made to take place, and at which the helium band spectrum was first seen (*i.e.*, the minimum voltage just before the occurrence of the discontinuity in the current-voltage relations), was the minimum radiation voltage 20.4. At high pressures the band spectrum and the orthohelium and parhelium series lines appeared simultaneously at this voltage. The band spectrum was never in any circumstances seen without the orthohelium and the parhelium series lines being seen also, though at the higher pressures it was relatively more intense with respect to these lines than at lower pressures.

The presence of the helium band spectrum at low voltages is shown in photographs 3, 4, 5 and 6. Nos. 3 and 5 were taken on a Wellington-Speedy plate, the time of exposure being 65 minutes for 3 and 80 minutes for 5. Nos. 4

and 6 were taken under conditions which were identical with those for Nos. 3 and 5 respectively, but on a Wratten panchromatic plate, the times of exposure being the same as for 3 and 5 respectively. The potential difference across the discharge tube for the photographs 3 and 4 was 21 volts, and for photographs 5 and 6 it was 14 volts, with an occasional fluctuation up to 16 volts. An immediate readjustment to 14 volts was made every time a fluctuation occurred.

In the band spectrum obtained in the experiments referred to in this section, the first doublet of the main series, and the first doublet of the second series, discovered by Fowler,\* were identified visually. The heads in the first main series doublet are at  $\lambda 4625\cdot4$  and  $\lambda 4648\cdot5$ , and the heads in the first doublet of the second series are at  $\lambda 5133\cdot3$  and  $\lambda 5108\cdot2$ . The details of the first main series doublet, given by Fowler, were clearly recognisable visually, and can be seen in photograph 3. In addition to these doublets, the prominent single-headed fluting at  $\lambda 5733$ , degrading towards the violet, recorded by Curtis† and by Fowler, was seen. All the heads down to  $\lambda 4546$ , recorded by Curtis, were also observed visually. Of these, the heads at  $\lambda 5733$  and  $\lambda 6399$  were the most prominent. These are present in photograph 4. When the external conditions controlling the discharge were varied in such a way as to make the band spectrum fade in brightness,  $\lambda 5733$  was one of the last lines to disappear, as judged from visual observations.

The results stated in this section show that the only limit which can be definitely associated with the helium band spectrum is the minimum radiation voltage, 20·4, and that this is only associated with it in that it has not been found possible *to excite* (as distinct from *to maintain*) the band spectrum of helium below this voltage. The view that the systems which give rise to the helium band spectrum are molecules formed by the combination of abnormal helium atoms, obtains support from the fact that the band spectrum was never observed in the absence of the orthohelium and parhelium series spectrum, and from the variation in the relative intensities of these two spectra with variation of the pressure of the helium. No evidence is afforded, however, as to the particular nature of the abnormal helium atoms concerned.\*

It follows from the above view that, when the band spectrum of helium is maintained below 20·4 volts, the number of helium molecules present cannot be increased without causing a reduction in the number of abnormal atoms present. The band spectrum of helium, like the series lines, has been

\* A. Fowler, 'Roy. Soc. Proc.,' A, vol. 91, p. 208 (1915).

† W. E. Curtis, 'Roy. Soc. Proc.,' A, vol. 89, p. 146 (1913).

maintained for prolonged periods below 20.4 volts, so that the number of molecules which are capable of giving rise to the band spectrum at these voltages, whether they are normal molecules, or molecules maintained in some abnormal condition, must remain constant in these circumstances.

Though the helium band spectrum was maintained down to the same limit as the orthohelium and parhelium series lines, it was not present in the spectrum of the discharge when the minimum voltage in the current-voltage relations had been passed, and the potential difference was increasing again in spite of all attempts to reduce it still further. As the voltage was being gradually reduced to the minimum value, both the series lines and the band spectrum diminished in intensity, the latter at a more rapid rate than the former. Sometimes only the heads of the bands, and not the detail, could be seen when the minimum value was reached. After passing the minimum value of the potential difference, the band spectrum had completely disappeared and the mercury line  $\lambda 5461$  stood out clearly, although it was much fainter than the brightest lines of the orthohelium and parhelium series.\* On further increasing the voltage, the line increased in intensity, reached a maximum brightness, and ultimately faded out entirely. The hydrogen line  $H_{\beta}$ , like the helium band lines, was not visible after passing the minimum value of the potential difference.

The changes in the spectrum, like the changes in the current-voltage relations which occur simultaneously, were found to be reversible, and after re-passing the minimum voltage on effecting the current-voltage changes in the reverse order, the helium band spectrum reappeared and the mercury line vanished. The disappearance of the band spectrum without the disappearance of the series lines, when the voltage was varied by altering the heating current, or the series resistance, and its subsequent reappearance when the variations of the controlling factor were made in the opposite order, admit of explanation in two ways.

The first explanation is analogous to the explanation of the maintenance of the series lines below 20.4 volts, by the presence of atoms maintained in an abnormal, more easily ionisable, condition, by the frequency of electronic-atomic encounters. It is possible that a somewhat similar effect occurs in the case of the helium molecules and that these, under intense electron bombardment, when no new molecules can be produced, are maintained in such a state of excitation that they are prevented from emitting the

\* It must be remembered that the carbon purifying tube attached to the discharge tube was immersed in liquid air during the experiment, so that the amount of mercury vapour present must have been very minute.

part of the band spectrum which falls in the region of the spectrum investigated.\*

The second possible explanation involves the assumption that a particular type of abnormal helium atom is essential for the production of the helium molecule, and that the constancy of the supply of molecules at any given values of the heating current and the voltage (below 20.4 volts) is maintained by the dissociation of a certain number of molecules into abnormal atoms and the formation of an equal number of new molecules. Clearly, in this case, the supply of molecules would decrease when the frequency of electron encounters with helium atoms reduced the supply of the particular type of abnormal atom required; hence the band spectrum would fade and eventually disappear, though it might reappear on reducing the electron bombardment. If this explanation is correct, one or more series of lines of the orthohelium and parhelium systems must disappear when the band spectrum disappears. Table III shows that none of the lines between  $\lambda$  7066 and  $\lambda$  4472 disappear under these circumstances, so that the series must be one having no lines within this region. The orthohelium principal series is the only series which fulfils this condition, and this is the one which results from transitions involving a return of the displaced electron to the 20.4 volts orbit. If the disappearance of this series at the same time as the helium band spectrum could be proved, evidence would be obtained not only in favour of the second explanation offered above, but also of Franck and Knipping's suggestion as to the nature of the helium molecule.

#### *Conclusion.*

It has been shown in the course of the foregoing pages that none of the orthohelium and parhelium lines can be excited without all of them being stimulated, and that the ionisation of the atom is essential for their production. With the exception of this fact, all the results of the present investigation, in so far as it is concerned with these lines and with the line  $\lambda$  4686 of the enhanced series, are in accord with Bohr's theory of radiation. The necessity for the occurrence of ionisation before the emission of the orthohelium and parhelium series lines can take place seems, however, to indicate some limitation of those electron transitions within the helium atom which involve an increase in the potential energy of the atomic system, not predicted by Bohr's theory. The limitation indicated is one which prevents direct transitions within the atom from the normal orbit to any orbits of either the crossed system, or the coplanar system, except the 2, S and the 2, s orbits.

\* The disappearance of  $H_2$  could be explained in a similar way, and it seems possible that the appearance of the mercury line  $\lambda$  5461, for a short stage in the current-voltage relations, may be another manifestation of a similar occurrence.



The results of the present investigation are thus directly opposed to the conclusion drawn by Franck and Knipping that the bends in their current-voltage curves in helium between 21.2 volts and 25.2 volts are due to the excitation of successive lines of an ultra-violet series, by the return of the electron after displacement to successive outer orbits of the helium atom. On the other hand, the results of the present investigation of normal uncharged helium are in complete agreement with the results of the investigations of McLennan and Ireton on the vapours of zinc, cadmium, and mercury, and of Foote and Meggers on caesium vapour.

The excitation of  $\lambda$  4686 at voltages above 50.8 volts, and not below this value, indicates that a similar limitation does not hold in the case of the stimulation of this line from a helium positive ion. It would be of interest to ascertain whether such a difference between neutral and ionised atoms occurs in other cases, for instance in mercury, zinc, or cadmium, vapour.

The conditions under which the band spectrum of helium made its appearance, and those under which it could be maintained, support the view that this spectrum has its origin in a helium molecule which is produced from abnormal helium atoms, and thus that it cannot be produced in normal helium for electron energies below 20.4 volts. The results of the present research afford no information regarding the energy which is necessary in order to excite the molecule to the emission of the band spectrum, beyond the fact that this energy can be acquired, under intense electron bombardment, at a potential difference of 20.4 volts. The results of the present investigation, however, considered in conjunction with the recent conclusions of Horton and Davies, namely, that at 20.4 volts some system is produced in helium which can be ionised by the radiation produced at 21.2 volts, support the suggestion made by Franck and Knipping that the coplanar atoms resulting from 20.4 volts electron collisions with helium atoms are capable of forming  $\text{He}_2$  molecules, which give rise to the band spectrum.

In conclusion, I wish to express my best thanks to Prof. F. Horton for his kind interest and advice during the course of this investigation.

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*Atmospheric Pressure and Refractive Indices, with a  
Corresponding Table of Indices of Optical Glass.*

By Lieut.-Colonel J. W. GIFFORD, F.R.A.S.

(Communicated by Sir Joseph Petavel, F.R.S. Received October 28, 1921.)

A new method of obtaining refractive index was described in 1902.\*

Instead of depending on the accuracy of arbitrary measurements of refracting angle or the accuracy of construction of a prism, this method was based on the mean value of the three angles of a triangle. The description of this method was accompanied by a Table of the principal refractive indices of quartz, calcite, and fluorite, obtained in this manner, and was followed later by similar Tables of the refractive indices of vitreous silica, water, and optical glass,† and in February, 1915, these were in turn followed by a Table of the refraction temperature coefficients of optical glass.‡

Since the error due to the method itself amounted to less than unity in the seventh figure, there was promise of great accuracy. But, nevertheless, with every care, and in spite of the correction for temperature, errors even exceeding unity in the fifth decimal place were frequently manifest, requiring repeated and tedious observation to eliminate. Hence suspicion fell on the barometer. But it was pointed out by the late Prof. Sylvanus Thompson, F.R.S., and afterwards by Sir Arthur Schuster, who indicated the lines to be worked on, that the modulus of rigidity of glass precluded its being sensibly affected by atmospheric pressure,‡ and that, therefore, any such effect must be due to the refraction of air alone.

It was evident that such influence was not altogether to be neglected, and a recent application of barometer readings as a correction for the variation of the refractive index of glass under pressure has made it clear that such effects exceed unity in the fifth decimal place and may therefore have significant value.

*Description and Application of the Correction.*

Formulae for the variation of the refractive index of air with temperature at given pressure have been given independently by MM. Benoit and Mascart, also by von Lang.§

\* 'Roy. Soc. Proc.,' vol. 70, p. 329.

† 'Roy. Soc. Proc.,' A, vol. 73, p. 201; vol. 78, p. 406; vol. 87, p. 189.

‡ 'Roy. Soc. Proc.,' A, vol. 91, p. 319.

§ Dufet, 'Données Numériques,' vol. 1, p. 78.

The mean of the constants given by Benoit and Mascart is 0.00374, and this has been adopted. It gives results which agree well with those obtained by von Lang's formula.\*

Let  $t$  = temperature recorded at observation.

$n$  = refractive index of air for the mean D line.†

Then  $n_0 = 1.0002923$  at standard pressure (760 mm.).

$$n_t - 1 = \frac{n_0 - 1}{1 + 0.00374t}.$$

The application of these formulæ for our purpose is as follows.

Let

$P$  = standard pressure }  
 $p$  = observed        „ } in mm. of mercury,

$n$  = refractive index of air at standard pressure and  
observed temperature,

$1 + \frac{(n-1)p}{P} = n' =$  refractive index of air at observed pressure and  
observed temperature,

$\mu$  = refractive index of glass at observed pressure and  
observed temperature,

$\frac{\mu n'}{n} = \mu' =$  refractive index of glass at standard pressure and  
observed temperature.

From this and two measurements of refractive index of the same wave-length, but at different temperatures, the refraction temperature coefficient at standard pressure for 1° C. may be determined.

Using this coefficient as a final correction, indices for other wave-lengths at standard pressure and observed temperature may be brought to standard pressure and temperature (15° C.).

\* Benoit's figures in the above formula are 0.00366*t*, Mascart's 0.00382*t*; von Lang's formula is

$$n_t = n_0 - 0.00905t + 0.00835t^2 \text{ (loc. cit.)}.$$

† The variation of the refractive index of air with difference of wave-length has been measured by Kaiser and Runge and given by Dufet (*loc. cit.*); it is small and may here be neglected.

Worked Example.

Obsn.

(1) Refractive index at 13.5° C. and 735 mm. bar. = 1.552267.

(2) „ „ 20.0° C. „ 769 „ = 1.552264.

(1)  $n = 1.0002783$ .

(2)  $n = 1.0002720$ .

$$1 + \frac{(n-1)p}{P} = n' = 1.0002691.$$

$$n' = 1.0002752.$$

$$(\text{At } 13.5^\circ \text{ C}) \mu = 1.552267.$$

$$(\text{At } 20^\circ \text{ C.}) \mu = 1.552264.$$

$$\frac{\mu n'}{n} = \mu' = 1.552253.$$

$$\mu' = 1.552269.$$

$$1.552269 - 1.552253 = 0.000016.$$

$$20.0^\circ - 13.5^\circ = 6.5.$$

$$\text{Hence temp. ref. coefft. at standard pressure} = \frac{0.000016}{6.5} = 0.00000246$$

for 1° C., and the refractive index at standard pressure and 15° C. = 1.552257.

As already described, the refractive indices for each wave-length required are corrected similarly for standard pressure and observed temperature, and are then brought to 15° C. by using the refraction temperature coefficient.

It must be stated here that whereas the refractive indices in the before-mentioned papers and in all previous papers were given at a temperature of 15° C., using a correction for temperature common to glass and air, it is only in the following indices that the correction for atmospheric pressure has been applied in addition. All indices, including those previously given are for glass in air, not *in vacuo*.

The refractive indices of a melting of fluor crown, whose temperature refraction coefficient was a minus quantity, have already been given.\*

In the fluor crown the indices of which are given above, this coefficient has changed sign, having apparently rounded the corner. In this connection it is perhaps interesting to recall the fact that the temperature refraction coefficients of fluorite, quartz, and vitreous silica all have the minus sign.

\* 'Roy. Soc. Proc.,' vol. 91, p. 319.

Refractive Indices of Glasses at Standard Pressure and 15° C., in Ascending Order of their Dispersions.

Designation*	Flint Crown. D. 591. Type 337.	Borosilicate Crown. C. 3537. Type 646.	Hard Crown. C. 4497. Type 9663.	Dense Flint. C. 3673. Type 1034. O'016030. ±0'000023. ±0'000022.	Dense Flint. C. 3467. Type 3743. O'016484. ±0'000012. ±0'000012.	Dense Flint. C. 1794. Type 572. O'016975. ±0'000011. ±0'000011.	Dense Flint. C. 4380. Type 3607. O'017166. ±0'000072. ±0'000075.
F - C = $\delta\mu$ .....	0'007330. ±0'000007. ±0'000008.	0'007970. ±0'000014. ±0'000015.	0'008663. ±0'000009. ±0'000009.	37'72. 37'72.	37'05. 37'05.	36'46. 36'46.	36'29. 36'29.
Probable error (1).....	67'42.	63'71.	59'95.				
Probable error (2)†							
$\nu = \mu - 1/\delta\mu$ .....							
Wave-lengths.							
A' 7682 K.....	1'489322	1'503146	1'514167	1'594820	1'600663	1'608662	1'612476
B' 7066 He.....	1'490722	1'504561	1'515673	1'597405	1'603293	1'611369	1'615186
6708 Li.....	1'491624	1'505525	1'516720	1'599193	1'605118	1'613247	1'617103
C. 6563 H <sub>α</sub> .....	1'492014	1'505939	1'517162	1'599696	1'605970	1'614125	1'618015
D. 5893 Na.....	1'494201	1'508325	1'519725	1'604584	1'610659	1'618983	1'622912
A. 5807 Pb.....	1'495353	1'509548	1'521086	1'607060	1'613209	1'621593	1'625566
5461 Hg.....	1'496031	1'510291	1'521863	1'608536	1'614713	1'623147	1'627141
E. 5270 Fe.....	1'496963	1'511313	1'522998	1'610622	1'616380	1'625383	1'629405
F. 4861 H <sub>β</sub> .....	1'499344	1'513918	1'525831	1'616026	1'622454	1'631100	1'635181
Φ. 4678 Cd <sub>2</sub> .....	1'500591	1'515280	1'527375	1'619011	1'623539	1'634261	1'638425
4415 Cd <sub>1</sub> .....	1'502675	1'517625	1'529932	1'624094	1'630750	1'639647	1'643919
G' 4341 H <sub>γ</sub> .....	1'503378	1'518353	1'530723	1'628717	1'632494	1'641364	1'645683
4046 Hg.....	1'506379	1'521723	1'534446	1'633401	1'640375	1'649502	1'653981

\* C = Chance Bros. and Co., Ltd. D = Derby Crown Glass Co., Ltd.

† (1) 'Roy. Soc. Proc.' vol. 70, p. 332. (2) 'Roy. Soc. Proc.' A, vol. 87, p. 189.

Note.—In the above table of refractive indices much accuracy is not claimed for the 6th decimal place, which, however, serves to determine the last unit in the 5th. The probable error is that of all the glass available, in each case, three different prisms having been taken at hazard from different parts of the melting ('Roy. Soc. Proc.' A, vol. 87, p. 190).

Table of Refraction Coefficients for 1° C. in each Melting.

Designation.	Temperature refraction coefficients.
Fluor Crown, D. 591 .....	0·0000005
Borosilicate Crown, C. 3537 .....	0·0000004
Hard Crown, C. 4497 .....	0·0000024
Dense Flint, C. 3673 .....	0·0000050
" " C. 3467 .....	0·0000040
" " C. 1794 .....	0·0000062
" " C. 4380 .....	0·0000062

Examples of the Application of Corrections for Temperature and Pressure.

Line.	Barometer.	Temperature.	Crude index.	Corrected for temperature.	Corrected for temperature and pressure.
	mm.	° C.			
A	758·3	14·375	1·489187	1·489185	1·489184 }
"	736·5	14·954	1·489195	1·489195	1·489182 }
F	756·2	12·639	1·631101	1·631116	1·631114 }
"	748·7	14·653	1·631122	1·631124	1·631117 }

*Note.*—Each pair of the above are for the same line and melting, but at different temperatures and pressures.

(*Note Added December 8, 1921.*)

#### *Errors due to Eccentricity of the Goniometer Circle.*

Since all refractive indices are practically affected alike by them, these errors are not of first importance, but may perhaps rank next to those due to atmospheric pressure.

The correction I have adopted is based on the formula for probable error (1) already referred to,\* but in this case the three "group deviations" are not taken for the formula  $\alpha$ . Instead three new groups are built up by adding together all deviations measured, respectively, when 0 of the circle is made zero, when 120 is made zero, and when 240 is made zero, no matter at what angle of the prism, provided that each angle is always represented in all three groups.

The values of those which show the greatest difference are now taken from it for  $x$  and  $y$  as before. Our formula then gives us the probable value of the eccentricity error in terms of the deviations, but we know not whether it is a *plus* or *minus* error.

The circle to which reference has been made is an 8-inch circle by

\* 'Roy. Soc. Proc,' A, vol. 87, p. 190.

Troughton. Another circle by Cooke, with a diameter of 18 inches, mounted on an instrument with 3-inch O.G., has been used throughout for check purposes, and also for experimental work on the refractive indices of water and of sea-water,\* and this circle is the more correct of the two.† Now this larger circle always gives a higher reading than the small one. Presumably then the error of the smaller circle must be additive.

The mean result in the index of some three hundred observations taken in this way amounted to 0·0000092, while the errors of observation taken over the same ground amounted to 0·00000085.

Taking these also as additive one to the other, we have a total error of 0·000010 for addition to the indices at the discretion of the user.

The advantage claimed for this method over any method which determines the total error due to the circle is, that that portion of the circle alone which has been put into use is put under contribution.

A complete measurement of index with all the observations, including the "group deviations" as ordinarily taken, is given in 'Roy. Soc. Proc.,' vol. 70, p. 338.

\* 'Roy. Soc. Proc.,' A, vol. 78.

† *Ibid.*, p. 408.

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**OBITUARY NOTICES**  
**OF**  
**FELLOWS DECEASED.**



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*William Gedding*

## WILLIAM ODLING, 1829-1921.\*

IN William Odling passed away the senior scientific Fellow of this Society. Elected sixty-two years ago, he may be said, like Nestor, to have lived through three generations of warring men; a front-rank fighter among the first, a member of the general staff during the second, an interested observer and wise counsellor at the end.

Perhaps the military metaphor which would best describe Odling's position as a young man in the great advance of international science, is that of interpreter and liaison-officer. The translator of Laurent's 'Chemical Method,' the pupil and enthusiastic disciple of Gerhardt, he formed one of the active band who developed the Theory of Types—a theory which brought with it, as a natural consequence, the recognition of the Rule of Avogadro, and thence the revision of the Atomic Weights, and led to the conception of Valency, and thence to the Periodic Classification of the Elements.

It was fitting that the Chemical Society, in celebrating its Jubilee in 1891, should have selected Odling to deliver an address on the chief developments of Chemical Theory since the foundation of the Society, and that he should have laid stress on the far-reaching effect of the work of Gerhardt and Wurtz, of Kekulé and Hofmann, of Williamson and Frankland, to the development of which he rightly claimed to have contributed "some little" share.

The son of a medical man, George Odling, practising in Southwark, William Odling was born there, September 5, 1829. In order to follow his father's profession, he entered, in 1846, Guy's Hospital, where he studied Chemistry under Dr. Alfred Taylor. In 1849 he passed the 1st M.B. of London University, gaining gold medals in Chemistry and in *Materia Medica* and Honours in Physiological Botany; and in 1851 he graduated M.B., obtaining Honours in Physiology and Comparative Anatomy. In the previous year he had been made Demonstrator in Chemistry at Guy's by Dr. Taylor, under whom he continued to work until elected Professor of Practical Chemistry. This chair he held until he succeeded Frankland as Lecturer in Chemistry at St. Bartholomew's in 1863. In 1848, in his twentieth year, he was elected to the Chemical Society, and seven years later he became one of the two secretaries; in 1869 he was made a Vice-President, and from 1873 to 1875 he served as President. At the time of his death he had been a member of the Council for an unbroken period of sixty-five years.

\* For several particulars in this Notice the writer has to acknowledge his indebtedness to the excellent and full account of Dr. Odling's life written for the Chemical Society by one of Odling's assistants, Mr. J. E. Marsh, Fellow of Merton College, Oxford, who writes (November, 1921) that he has just seen a record of Odling lecturing on chemistry to his school-fellows while still at school.

Although he gave some assistance to his father, he does not appear to have contemplated making a practice for himself, and, with the exception of carrying out the duties of a Medical Officer of Health, he confined himself to pure and physiological Chemistry.

In 1854 he published his first book, 'Practical Chemistry for Medical Students,' and in the following year became known as the translator and editor of Laurent's 'Chemical Method,' and—through his first lecture at the Royal Institution—as a gifted exponent of the new doctrines.

In translating Laurent, the two-volume system of Gerhardt (finally adopted by his colleague) was used systematically by Odling. "The distinction," he writes in his preface, "between the system of equivalents ordinarily adopted in this country, and the two-volume notation adopted in this work, may thus be expressed. In the new system the atomic weight of carbon is 12, of oxygen is 16, of sulphur is 32; all the other atomic weights are unaltered."

By this method the modern formulæ for water, ammonia and methane were introduced, and they carried in their train the correct formulæ for many simple bodies; but the dyad metals were still written with their "equivalent," *i.e.*, with half their modern atomic weights. In his 'Manual of Chemistry,' published in 1861, he still adopted the same formulæ, and this may be one of the reasons why the Manual was never completed. Under the influence of Williamson, he became converted to the complete reform urged by Cannizzaro, and for many years he was one of the chief expounders of the "New Chemistry."

In 1868 Odling was appointed Fullerian Professor of Chemistry at the Royal Institution in succession to Faraday, and a number of his contributions to Science are in the form of abstracts of his discourses delivered at the Institution. In 1872 he was elected Waynflete Professor of Chemistry at Oxford, in succession to Sir Benjamin Brodie; he held the chair for forty years, until his resignation in 1912. In 1883 he became President of the Institute of Chemistry, which obtained its Charter during his term of office, largely owing to his advocacy.

His presidential address to the Institute gave rise to some sharp criticism. It was the time when the cry for the endowment of research had been taken up in many quarters, and Odling maintained that the discipline of having to earn one's daily bread is wholesome, and is no impediment to the achievement of the highest things—and that the best of all endowments for research is that with which the searcher succeeds in endowing himself. It was easy for him to instance many chemists distinguished in research, who—like Odling himself—had obtained success as expert advisers and witnesses, or, to use his own phrase, had reached "professional eminence"; but it was perhaps unfortunate that he should advise the young men of the Institute to pursue research for which many of them "in the seed-sowing time of their life" would be willing to make "considerable professional sacrifices." Such phrases were, of course, fastened on, and even given a personal reference.

Odling replied, with some excusable bitterness, that he was addressing a body of *professional* chemists, and not proclaiming to students "the whole duty of a chemist."

At Oxford Odling maintained his reputation as a lecturer. He aimed at systematising and co-ordinating the researches of others, and bringing them into their place in an ordered system. He was not without aptitude for and skill in experiment, but the experimental side of chemistry did not appeal to him. The laboratory was provided with a University teacher—the Aldrichian Demonstrator—and Odling brought with him another demonstrator, and to these the practical instruction of students (and their fees) were assigned; it was not etiquette, Odling said, for the Professor to enter the Chemical Laboratory.

This was a set-back from the practice and example of Brodie, who, from his appointment in 1855, had been busy with his own hands, and had guided and encouraged his assistants to undertake researches of their own. It was not that Odling *discouraged* research: on the contrary, he was glad to help and give facilities to research workers, and his well-stored memory was often useful in recalling what had been done in foreign (especially French) laboratories. To show that important work was done in his laboratories, it is only necessary to recall the pioneering researches of F. D. Brown on the theory of fractional distillation, and the investigations of J. E. Marsh on camphor and the terpenes. But the fact remained that Odling founded no school—to which charge he might plead that it was not his *métier* to do so; that he had been elected, not as an experimenter, but as an exponent of chemical theory, and that he had been true to his past record.

At Oxford Odling took an active part in University affairs and served on the Hebdomadal Council for 15 years. He spoke incisively and well in Congregation, and for his successful opposition to one proposal he should be gratefully remembered by Oxford men of Science. The difficulty of "Compulsory Greek" was already being felt, and in 1879 a plan was put forward to get round the difficulty by creating a new degree in Natural Science, which might be obtained by science students without passing in Greek.

The new degree opened no avenue to the M.A. degree, and therefore debarred the holder from being a member of Convocation—the governing body of the University. This privilege was reserved for the B.A.—the man who had, or once had had, the necessary smattering of Greek—for "Greek," as Canon Liddon urged in the *Times*, "imparts those habits of exactness and refinement, without which it is impossible to reach the higher characteristics of an educated man." Odling's common sense had little difficulty in refuting these arguments, and in persuading his Oxford colleagues to reject the proposal: it was better to endure compulsory Greek—however useless for culture the smattering required might be—than lower the dignity of the school of Natural Science. Compulsory Greek, as all men know, died hard at Oxford, but Odling lived to see the end.

It was in 1875 that the writer, then an undergraduate, first attended Odling's lectures in the Oxford Museum, and had the privilege of meeting, at his house in Norham Gardens, Hofmann, Frankland and other chemists. His lectures were possibly more appreciated by graduates—college tutors and coaches—than by those in *statu pupillari*; the writer certainly appreciated them more when he in turn became a teacher.

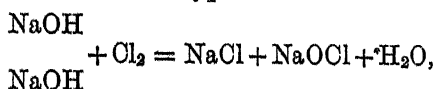
Odling's lectures were always attractive—as good summing-up is attractive. The arguments were marshalled with admirable precision, the reasoning was clear and convincingly given, the scope of the discourse strictly confined to the matter in hand. Here was the dry light of Science permeating an abstruse problem, where no human element, no clash of personal views, no stimulating conjecture, no "thinking aloud" seemed to be in place. His hearers felt that the "thinking" had been done beforehand, and that what they were listening to was the considered judgment of the court.

In symbolising constitutional formulæ most men look for some design by which the parts are mechanically joined; but to Odling this seemed unnecessary and misleading. Hence the mechanical bonds of Frankland became in Odling's notation mere dots or dashes attached to an atom or radical, marking what he called its "desmicity" or combining power. Odling, indeed, was a little bitter on the misuse of "bonds" in graphic notations. "Such a system," he writes in the preface to his 'Outlines,' "used to express with equal confidence the ascertained and unascertained constitution of all bodies whatsoever, has I believe exerted and still continues to exert a most prejudicial influence on the study of Chemical Science, by making the fanciful sticking-together of variously pronged discs of more importance than the investigation of phenomena."

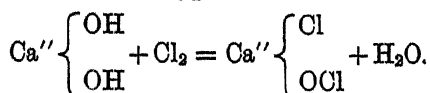
The Type Theory, which owed so much to Odling's powerful advocacy, became in his mind something far more fundamental than a conventional mode of regarding chemical combinations. The types themselves—water, ammonia, methane—by reason of their composition and structure, were endowed with certain enduring properties that were retained by their derivatives. While the setting up of imaginary structure was freely practised by chemists, the possibility already existed of determining *relative* structure—"of making out that in one body the structural arrangement is similar to, or different from, that of another and usually more simple body." Here is a sentence from a Royal Institution Lecture of 1869; there could be no mistaking the speaker:—"Marsh-gas is transformable into methyl chloride by the action of chlorine; and methyl chloride into marsh-gas by the action of hydrogen. From this mutual metamorphosis, and from the parallelism of their properties, formations and transformations, the two gases are inferred to have one and the same molecular structure, whatever that may be."

Believing, as Odling did, that the structure of molecules was un-ascertainable, or at all events not yet ascertained, he abstained from structural formulæ and relied on similarity of reactions to indicate similarity of composition. Thus in the "Outlines" we find his much-quoted formula for

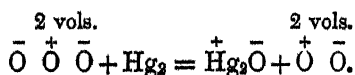
bleaching powder introduced by a simple analogy without further explanation. Just as chlorine acts on the hydrate of a monad metal to form a molecule of the chloride and a molecule of the hypochlorite :—



so chlorine acts on the hydrate of the dyad metal calcium to form a condensed molecule—half chloride and half hypochlorite :—

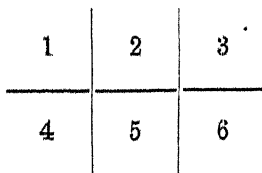


The simple explanation of Andrews' work on the molecular constitution of ozone was given by Odling in his "Manual," published the year after the 'Phil. Trans.' memoir by Andrews. If ozone is a compound of oxygen with oxygen and the contraction be consequent on their combination, then if one portion of the combined oxygen were absorbed by the reagent, the other portion would be set free and by its liberation might expand to the volume of the whole. Thus if we suppose three volumes of oxygen to be condensed by their mutual combination into two volumes, then on absorbing one-third of this combined oxygen, the remaining two-thirds would be set free, and consequently expand to their normal bulk, or two volumes :—



In his Oxford lectures hydrogen was no longer the *quasi* metal imagined by Graham; it was the "vanishing point of the hydrocarbons," and would resemble them on liquefaction.

Again, the benzene hexagon of Kekulé, and the structural derivatives of Körner and others, became in Odling's hands two superposed triangles, each of three carbon atoms, flattened for representation into two lines :—

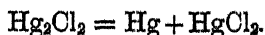


Odling's views on the relation of the elements as revealed by their atomic weights were much in advance of those of his contemporaries, and led him almost within sight of the Periodic Law. With his strong regard for analogies, he clearly marked out the parallelism of successive groups or "families" of elements, and in comparing, for instance, the carbon with the nitrogen family, he plainly showed that a tetrad element was missing, with an atomic weight about 72, corresponding with arsenic (75) in the neighbouring group. This prediction of germanium was made long before Mendeléeff's periodic classification was known in England.



The question of the position of aluminium in the natural classification of the elements led to the preparation of aluminium methide and ethide by Buckton and Odling, in order to determine the vapour density of some volatile compounds of the metal. Following a suggestion of Cahours, they prepared the two compounds by heating aluminium with the methide and ethide of mercury in sealed tubes at 100° C. The aluminium ethide boiled at 194°, and its vapour density was found to be 4.5 (compared with air) at 234°, the formula  $\text{AlEt}_3$  requiring 3.9, and the double formula,  $\text{Al}_2\text{Et}_6$  requiring 7.8; similarly, aluminium methide had a vapour density 2.8 at 240°, the theoretical value for  $\text{AlMe}_3$  being 2.5. It was found that the vapour density increased with diminishing temperature, and the vapour density of the methide, determined near its boiling point (130°), was 4.4, approximating to the theoretical density for  $\text{Al}_2\text{Me}_6$ . This increase of vapour density explained Deville's results with aluminium chloride, and the research showed the essentially triad character of aluminium.

Another research on anomalous vapour densities, though it does not appear that he published it, was due to Odling. The vapour density of calomel was found to correspond to the simple formula  $\text{HgCl}$ —a fact which contradicted the law of odds and evens (Odling's Perissads and Artiads). The chemical depravity shown by vapourised calomel is shared by other compounds (nitric oxide is a notorious offender), and we have learnt to be more lenient in our judgments; but in the early days of the new chemistry such conduct was anathema and had to be explained away. Odling showed by suspending gold leaf in the vapour of calomel that mercury amalgamated with the gold, and the anomalous vapour density was explained by the dissociation of the real molecule into mercury and the higher chloride:—



Concerning the anomalous vapour density of ammonium chloride, Odling disputed the "ammonium" theory, and argued that ammonia maintained its identity and formed a molecular compound with  $\text{HCl}$ , just as it did with  $\text{AgCl}$ , and the two compounds were broken up on heating in the same way. Why, asked Odling, should the chlorine atom leave the hydrogen atom, for which it has such a strong affinity, to attach itself to the nitrogen atom, for which it has so little? The chlorine does not do so, replied Williamson, but it leaves *one* hydrogen atom to attach itself to a nitrogen atom holding *four* hydrogen atoms together; the group containing four hydrogen atoms has greater attractions than a simple atom.

But though Odling might sometimes carry an analogy too far, there can be no question of the effective use he made of the weapon. Few of his students can forget the convincing way he pleaded for the "normal" character of ortho-silicic acid. Compare the normal hydrides of chlorine, sulphur, and phosphorus, formed on the three well-established types, and consider the acids formed from them by the fullest oxidation:—



These are the normal fully oxidised, or ortho-acids: must not the hydride of silicon have a corresponding normal ortho-acid:—



This was the basis on which Odling built up a classification of the silicates, parallel with the ortho-, pyro-, and meta-phosphates. Odling, when examining *vis à voce*, once asked a candidate what he meant by a "normal acid," and the prompt reply was, "Ortho-nitric acid,  $\text{H}_3\text{NO}_4$ , is a normal acid." To this the examiner remarked, after a pause, "I cannot contradict you."

In 1872 Odling married Elizabeth Mary, daughter of Alfred Smee, well known as the inventor of Smee's cell, and perhaps more widely known as the author of 'My Garden.' Mrs. Odling died two years ago, and three sons of the marriage survive their parents, the eldest having added his grandfather's name to his surname.

Odling resigned the Waynflete Chair in 1912, after a tenure of 40 years; he was succeeded by Dr. W. H. Perkin, F.R.S., Professor of Organic Chemistry in the University of Manchester.

It was his privilege to be a guest at two Jubilee banquets given by the Chemical Society to the Past-presidents who had been Fellows for 50 years; the first in 1898, when he was ranked in the toast with Williamson and Frankland as one of the founders of the New Chemistry; and again, in 1910, when, as the *doyen* of the Past-presidents, he asked to speak after his younger colleagues—Roscoe, Crookes, Hugo Müller, and Vernon Harcourt—had replied. All these colleagues he survived, and almost lived to hear—this year—a third generation answering to their Jubilee toast. He kept up a keen interest in Science to the end.

H. B. D.

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## ALEXANDER MUIRHEAD, 1848-1920.

ALEXANDER MUIRHEAD was born in 1848, the second son of John Muirhead, a farmer in East Lothian. At the age of three his nurse fell when carrying him, and he received a blow on the head which made him permanently, though partially, deaf. As a child he was thought rather stupid because he wished to know the reason of everything before doing it, and an experiment recorded against him is the planting of a toy spade in the garden in order to grow a second one.

His father, while still a fairly young man gave up farming, brought his young family to London, and started telegraphic work, with Mr. Latimer Clark as partner, in Regency Street, Westminster. Young Alexander now went to University College School, Gower Street, where he soon began to carry off prizes. Chemistry came to him very easily, and he went on to the College, where, in mathematics, he had the advantage of the teaching of De Morgan, of whom he became a devoted pupil, and by whom he was imbued with the spirit of accuracy. He often spent his school half-holidays in his father's works, where he sometimes felt the inspiration of seeing Clerk Maxwell and Sir William Thomson.

Instead of going to Cambridge, his father sent him to study Chemistry under Dr. Matthiessen at St. Bartholomew's Hospital, but before his pupilage had expired, Mr. Latimer Clark borrowed him to work out the problem of a cell for standard voltage in the firm's laboratory. This was the beginning of an immense amount of accurate work in connection with electrical standards, and he may be said to have inaugurated the standards of Capacity. He graduated B.Sc., with honours in Chemistry, in 1869, obtained the Doctorate in 1872 in Electricity, and began a life-long friendship with Prof. Carey Foster. He now became scientific adviser to his father's firm, where John Perry and some others also worked as his assistants, because at that time it was the centre of accurate pioneering work in practical electrical measurement in association with Charles Hockin and others.

In 1875 Dr. Muirhead invented his artificial line with distributed capacity, and succeeded in the notable achievement of duplexing cables; his own personal experimental work being done chiefly at Aden. After this success, he initiated a private laboratory for research work, first in Cowley Street, Westminster, and afterwards near Storey's Gate. Here he perfected his electrical standards; and about 1896 he began the manufacture of instruments at Elmers End.

In 1894 his attention was directed to the possibility of telegraphy by means of Hertzian waves, through hearing a lecture at the Royal Institution in May of that year; and work was done for years at Elmers End towards the development of this subject, especially in the obtaining of messages recorded on siphon-recording tape, instead of being merely heard in a telephone.

Accurate tuning was subsequently accomplished, and disturbances from neighbouring experimental stations were eliminated, partly by the avoidance of earth connection; a subject on which a paper was communicated to the Royal Society in 1909 ('Roy. Soc. Proc.,' A, vol. 82, pp. 240-256). It was possible not only to hear, but automatically to record messages from a distant station while another sending station was active within about a hundred yards of the receiver. Automatic receiving is a severe test, since a machine does not discriminate and ignore, as a human receiver can.

In 1904 he was made a Fellow of the Royal Society, and was put on the board of the National Physical Laboratory, to whose Director he ultimately yielded the custody of the electrical standards of capacity, which he had watched over and maintained with anxious care. But a slight stroke of paralysis in 1909 caused additional weakness of body. The war was a still further strain, and he felt acutely his inability to serve the country as he earnestly desired. On the 13th December, 1920, he passed quietly away, his remains being laid in the family grave at West Norwood.

He was a man who achieved much under exceptional bodily disabilities; and his devotion to accuracy was of great service in the development of cable telegraphy. His instruments were beautifully designed and constructed, and all measurements were made and recorded with scrupulous care. His character was of the highest, and by his friends he was much beloved; while the pertinacious enthusiasm with which he had overcome difficulties sufficient to daunt ordinary men could not fail to arouse feelings of admiration even among those who but slightly knew him. In 1891 a severe attack of influenza left him permanently lame, and for years subject to acute pain, of which few outside his home knew, so well did he conceal it.

He married Mary Elizabeth, daughter of Mr. William Blomfield, of Upper Norwood, in 1893.

O. J. L.

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## ERRATUM.

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Page 111, line 5, shift equation-number (2) to the line above.

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